MODELS FOR THE KRAFT PULPING OF EUCALYPT, PINE AND BINARY CHIP BLENDS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By

MOHAMMAD IDREES

to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

MARCH, 1982

DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the present work "MODELS FOR THE KRAFT PULPING OF EUCALYPT, PINE AND BINARY CHIP BLENDS" has been carried out under my supervision and that the work has not been submitted elsewhere for a degree.

March 12, 1982

(Dr.) Hariharan Veeramani
Professor
Department of Chemical Engineering
Indian Institute of Technology
Kanpur-208016, INDIA

ACKNOWLEDGEMENTS

The author expresses his deep sense of gratitude and indebtedness to Dr. H. Veeramani for his guidance, interest and constant encouragement throughout the course of this investigation.

The author thanks Mr. U.L. Saksena and Mr.L.N. Chowdhary (Star Paper Mills Ltd., Saharanpur) for providing laboratory and pulp testing facilities.

The author thanks Mr. Santokh Singh of the Department of Mathematics for his help in the regression analysis of data and Mr. Bahadur Singh for his cooperation during the course of experimental work.

Finally, the assistance of Mr. D.S. Panesar and Mr. B.S. Pandey in the preparation of this report is also acknowledged.

M. Idrees

CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

AA	Active alkali, % Na_2O o.d. basis
b_o	Intercept (constant term) in the model
b_i, b_j, b_{ij}	Parameters in the model
$\underline{b}$	Vector/matrix of parameters
D	Liquor-to-wood ratio
EA	Effective alkali, % Na_2O o.d. basis
f	Functional relationship
F	Fisher ratio (F-ratio)
H	H-factor
k	Number of variables (factors)
K	Kappa number
n	Number of repeated experiments, exponents
N	Total number of experiments
p	Number of parameters (coefficients)
P	Permanganate number
R^2	Multiple correlation coefficient
s.d.	Standard deviation
s_i^2	Error variance of ith experiment
s_y^2	Experimental error variance
s_v^2	Estimated variance
s_{ad}^2	Variance of the model
S	Sulfidity, %
$\underline{S}$	Least square objective function

SSR	Sum of squares due to regression
SST	Sum of squares corrected total
t	Pulping time at maximum temperature, min
't'	"Student's t " value
t_h	Time to maximum temperature (heating time), min.
T	Pulping temperature, °C
v_i	Variation interval of the ith variable
x_i	Coded value of ith variable (factor)
x_1	Coded value of chemical charge (AA)
x_2	Coded value of temperature
x_3	Coded value of sulfidity
x_4	Coded value of liquor-to-wood ratio
x_5	Coded value of time-at-temperature
x_6	Coded value of chip thickness (size)
x_7	Coded value of time-to-temperature
x_8	Coded value of pine fraction
$\bar{x}$	Average (mean) value
$\underline{x}$	Design matrix
X_i	Actual value of ith variable (factor)
X_{io}	Actual value of ith variable at the central point conditions
$\underline{x}^T$	Transpose of matrix $\underline{x}$ or vector
y	Response
Y	Pulp yield, %
Y_t	Total pulp yield, %

Y_s	Screened pulp yield, %
Y_r	Screen rejects,%
y_i	Response (output variable) of ith experiment
y_i'	Corresponding value of response predicted by the model
$\bar{y}$	Average (mean) value
$\underline{y}$	Vector of observed responses

MODELS FOR THE KRAFT PULPING OF EUCALYPT, PINE AND BINARY CHIP BLENDS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the degree of

DOCTOR OF PHILOSOPHY

by

MOHAMMAD IDREES

to the

Department of Chemical Engineering
Indian Institute of Technology, Kanpur

March, 1982

SYNOPSIS

This study deals with the kraft pulping behaviour of (a) plantation grown (8-10 years old) eucalypt (Eucalyptus tereticornis hybrid), (b) abnormal (twisted) chir pine chips (Pinus roxburgii var. longifolia), and (c) blends of eucalypt-pine chips.

The major pulping variables considered include: chemical charge, temperature, sulfidity, time-to-maximum temperature, time-at-temperature, liquor-to-wood ratio and chip size. The dependent variables studied include: yield, Kappa number (pulp lignin content), black liquor solids, and strength properties-tear index, burst index and tensile index. All the experiments were conducted with manually

screened handsorted mill cut chips in a 15 liter rotary digester using 2.5 kg (ovendry basis) chips per batch.

The effects of time-to-temperature (60-120 min) and chip size were studied by simple factorial designs and the data analyzed using Yates's algorithm. Strong interactions between time-to-temperature and temperature favoured a longer heating period and lower pulping temperature to improve the yield of screened pulp. Screen rejects was negligible for eucalypt pulp and was below 2 per cent for pine. Chip size is not a significant variable for pulping eucalypt (average thickness 2-6 mm) while a lower thickness (3-4 mm) improved the yield of screened pine pulp. A constant temperature rise period (90 min) and screened chips with average thickness of 3-4 mm was selected for all the subsequent experiments.

The main experimental design was selected to study the effect of the remaining five pulping variables. A second-order central composite rotatable design (Box and Hunter) requiring 32 experiments was used for eucalypt chips with - chemical charge (14-18 per cent active alkali as Na_2O), temperature (155-175°C), sulfidity (15-27 per cent), liquor-to-wood ratio (3.0 - 4.2) and time (30-90 min.). One half replicate of a 2^5 factorial design with six replicate runs at central point conditions (22 experiments) was selected for pulping pine chips with - chemical charge (16-19 per cent as Na_2O), temperature (165-175°C), sulfidity (20-30 per cent), liquor-to-wood ratio (3.5-4.0) and time (60-100 min.).

Experimental data was correlated by second-order regression equations by response surface methodology using a digital computer (DEC system -1090). Regression analysis for both eucalypt and pine gave good correlation for yield, Kappa number, black liquor solids and active alkali consumption.

Eucalypt pulp yield was most dependent upon chemical charge besides pulping temperature and time. The yield of pine pulp was dependent upon chemical charge, temperature and sulfidity. Eventhough sulfidity has no direct effect on eucalypt pulp yield, it showed strong interactions with time, temperature and liquor-to-wood ratio. Kappa number of both eucalypt and pine pulps is influenced by chemical charge, temperature and time; interactions of sulfidity with temperature and time are also significant. The contribution of the other pulping variables were relatively less for the two species.

Beating characteristics show that both the pulp types must be beaten to 40°SR to develop the potential strength properties-tear, burst, tensile and folds, even though slight beating (20°SR) of pine pulps gave a maximum tearing resistance. Regression models for strength properties gave a satisfactory correlation coefficient ($R^2 = 0.7 - 0.8$) for eucalypt and pine pulps except the tear index of the latter.

The models developed were used to locate the optimum conditions for pulping eucalypt and pine by the 'Constrained

Rosenbrock method' and the estimates were confirmed experimentally. The models are graphically illustrated to depict the responses by univariate representation and two-dimensional contour plots.

The final phase of this study considers pulping binary chip blends in a 3-compartment digester using a factorial design with - pine fraction (0.1, 0.3), chemical charge (16, 18 per cent as Na_2O) and temperature (165, 175°C). The data are correlated satisfactorily by a regression equation and showed good agreement with the estimates based on the models developed earlier for the component species.

In this study statistical experimental designs have been successfully used to develop mathematical models for the kraft pulping of eucalypt, pine and binary chip blends. Eucalypt pulping experiments cover an adequate range of the pulping variables; the range selected for pine and chip blend experiments have a bias towards the range adopted for eucalypt, constituting over 70 per cent of the digester furnish. The models can be used to estimate the variations in pulp characteristics caused by changes in the pulping variables over the experimental range of this study.

Further work is recommended dealing with binary chip/pulp blends and beating characteristics to determine the optimum proportions giving the desired strength properties.

CHAPTER 1

INTRODUCTION

Softwoods consist of long fibers(average length 3-5 mm) suitable for making paper with good strength propertie The conventional softwood species like pine, fir, spruce, etc. are located in relatively inaccesible areas in the Himalayan region and are not available at economical prices to the paper mills. Consequently bamboo has become the principal source of long fiber pulp for the paper industries in this country. In the past two decades efforts to conserve the available bamboo resources have established the use of increasing quantities of mixed hardwoods or plantation grown eucalypts (hardwood) to the extent of about 50 per cent of the digester furnish in many bamboo based paper mills. In some states like Uttar Pradesh, Karnataka, Tamilnadu, well developed eucalypt plantations supply regular pulpwood to the mills. In the past 10-15 years, plantation grown eucalypt (8-10 years old) have become an important pulping raw material Fast growing hybrid varieties of eucalypts are now used for making paper pulp (E. tereticornis, E. globulus) and rayon grade pulp (E. globulus, E. grandis) in the above states. The eucalypt pulp is used in admixture with bamboo or pine kraft pulp for obtaining the desired paper strength properties

The hybrid species of eucalypts comprising of E. robusta and E. tereticornis (mainly E. tereticornis) has been gradually introduced as a suitable fiber resource for paper making. Large scale plantations of E. tereticornis hybrid (Mysore gum) have been developed in Najibabad, Kotdwar, Jawalapur, and Pathri divisions of Uttar Pradesh to supply pulpwood. Uttar Pradesh is devoid of bamboo resources and the limited quantities of chir pine (Pinus roxburgii syn. longifolia), available as residuals of forest lumbering operations in adjoining regions is used to supply the long fiber pulp necessary to augument the strength characteristics of eucalypt pulp. The available pine wood consists mainly of abnormal portions of the tree like irregular shaped branches, stems and knots (termed as twisted chir pine). The chips from such diverse portions of the tree will have an abnormal chemical composition, fiber morphology and pulping behaviour compared to the chips from the normal pine pulpwood (stems).

This investigation deals with the kraft pulping of chips from plantation grown eucalypt (E. tereticornis), abnormal (twisted) chir pine (P. roxburgii) and binary chip blends for Kappa number of 25-60 suitable for making wrapping papers.

Eucalypt species native to Australia are now grown in several countries. Watson and Cohen (1969) have given a historical survey of the technical literature upto 1969 dealing

mainly with the pulping characteristics of native eucalypt species and the efforts on utilisation of plantation grown eucalypts by various countries - India, Spain, Portugal, Morocco, Italy, Southern Africa, Southwestern U.S.A. and Brazil. The mature/overmature native mixed eucalypt species have a broad age distribution and contain a high concentration of polyphenolic extractives (kino veins) and cause unusual problems during pulping and chemical recovery operations (Smith, 1965; Phillips et al., 1967; Watson and Cohen, 1969; Higgins, 1970; Oye and Mizuno, 1972; Oye et al., 1973).

Introduction of plantation grown eucalypt as pulpwood for paper mills being of recent origin, published information is meagre. Some preliminary investigations by Guha(1968, 1973, 1975), Foelkel, 1980, Hannah et al(1977), and Franklin (1977) are reported in regard to the suitability of plantation grown eucalypts for wrapping and writing papers. In view of the potential promise for large scale utilisation of plantation grown eucalypts for paper making, a detailed study is initiated to investigate the kraft pulping characteristics. The pulping characteristics of young plantation grown eucalypts would be different compared to the native mature Australian eucalypts owing to the differences in the physico-chemical characteristics. The quality (strength properties and residual lignin - Kappa number) and quantity (yield) of the eucalypt pulp produced are

governed by the following important variables of the kraft digester system: chemical charge, pulping temperature, sulfidity, time of heating the digester to maximum temperature, time of cooking at maximum temperature, liquor-to-wood ratio and chip size.

The nature of the heterogeneous kraft pulping reactions are quite complex for the development of a satisfactory theoretical/mechanistic model of the kraft pulping process. Consequently, empirical models are usually proposed for kraft pulping to enable a meaningful interpretation of the influence of the different variables and correlation of the observed data. A better understanding of the kraft system also would ultimately lead to satisfactory process control of digester operation.

Statistical experimental designs are used to study the effects of different pulping variables. Simple factorial designs are adopted to study the effects of chip size (thickness) and the time to raise the digester to the desired pulping temperature and to select suitable constant values for the subsequent experiments. The effects of the remaining five pulping variables are studied by a sequential experimental design consisting of fractional factorial design, replicate determinations at central point conditions and additional experiments at star points to form a second-order central composite rotatable design. The experimental data are used

to develop satisfactory and reliable second-order regression equations correlating the observed responses (yield, Kappa number, black liquor solids, burst index, tear index and tensile index) with the significant pulping variables. These models are used to predict optimum pulping conditions for eucalypt and checked experimentally. The models for eucalypt pulping are graphically represented to illustrate the effects of different variables about the central point conditions as well as by two-dimensional contour plots for the responses with chemical charge and temperature as the dominant variables.

Similarly the kraft pulping characteristics of the abnormal pine chips are studied using simple factorial designs to determine the effects of the pulping variables and develop regression equations for pulp yield and Kappa number. The regression equations for pine are utilized for the prediction of the best pulping conditions and interpretation of the effects of the different variables similar to the methods adopted for eucalypts. Proximate analysis of eucalypt and pine wood meal samples, pulp fiber dimensions and beating curves are used in the interpretation of some of the observed effects.

Pine kraft pulp (softwood) would give superior tearing strength and folding endurance while eucalypt kraft pulp (hardwood) will give good formation and smooth surface to the

paper. A blend of eucalypt and pine pulps should give a paper of the desired strength properties incorporating the superior qualities of both the softwood and hardwood pulps. The composite pulp of the desired strength properties can be obtained by (1) blending varying proportions of refined pine and eucalypt pulps, (2) blending of separately beaten eucalypt and pine pulps, or (3) pulping binary chip blends. This study includes a preliminary factorial experimental design in a 3-compartment digester for the simultaneous pulping of pine, eucalypt and binary chip blends with chemical charge, temperature and pine fraction as the variables. The results for the three pulps are compared with the estimates based on the regression equations developed earlier for eucalypt and pine and the weighted average values for the blends from the estimates for the component pulps. Regression models are also obtained for the pulping of binary chip blends.

An outline of the various chapters of this dissertation is given below:

Chapter 2 presents a review of the nature of pulping reactions, influence of fiber morphology, effects of pulping variables, kinetics of delignification reactions and a summary of the empirical models proposed for kraft pulping of softwoods and hardwoods.

Chapter 3 presents the methodology adopted for statistical experimental designs to develop regression models for kraft

pulping to correlate pulp yield, Kappa number, and strength properties with the significant pulping variables. The methodology of multivariable constrained optimization (Complex method of Box and Constrained Rosenbrock method) is also outlined.

Chapter 4 gives details of the experimental methods used for pulping, proximate analysis, fiber morphology and pulp properties.

Chapter 5 presents the results and discussions of this investigation in three parts.

Section 5.1 considers simple factorial designs and second-order central composite rotatable design to assess the influence of the major pulping variables to obtain satisfactory regression models. These models are used for the determination of significant pulping variables, optimum pulping conditions and for the graphical representation of the response surfaces.

Section 5.2 discusses the pulping behaviour of pine using simple factorial experimental designs and regression analysis of experimental data to develop satisfactory models.

Section 5.3 deals with regression models for the pulping of binary chip blends and estimates for composite pulps based on component pulp properties.

A summary of the pulping characteristics of eucalypt, pine and chip blends is presented in Chapter 6 which also includes recommendations for further work dealing with the binary system.

CHAPTER 2

PULPING VARIABLES AND MODELS FOR THE KRAFT SYSTEM - A REVIEW

2.1 Kraft Pulping Process:

Wood is the preferred raw material for making pulp and paper. Liberation of the constituent fibers of the wood chips is the primary objective of the pulping process. Wood is pulped mainly by the kraft process with sodium hydroxide and sodium sulfide (white liquor) as the active pulping chemicals. Kraft pulping is suitable for several softwood and hardwood species and is economical with efficient recovery of pulping chemicals and energy from the spent liquor.

Cellulose and hemicelluloses are the principal plant polysaccharides constituting upto 65-75 per cent of the wood material; the remainder consists mainly of lignin (25-35 per cent) and a small amount of extractives. The major chemical constituents of wood are all polymeric in nature. Cellulose is a linear polymer of β-D-glucose with a large degree of polymerization (DP = 5000 - 10,000). Lignin is a three dimensional amorphous network polymer based on phenyl-propane monomers. Softwood lignins consist of guaiacyl propane units as monomers while hardwood lignins are derived from varying proportions of guaiacyl-propane and syringyl-propanoid units. Hemicellulose is a linear hetero-polymer of glucose, mannose,

xylose, galactose etc. and the degree of polymerization is low (DP 200). Cellulose alone is fibrous and consists of both crystalline and amorphous regions. In a fiber, cellulose can be viewed as the structural element, hemicelluloses as the matrix substance and lignin as the encrusting material.

Figure 2.1 depicts the common gross structural aspects of the different layers of the fiber wall of a typical softwood tracheid and a hardwood fiber. The fiber has a thin primary wall (P) around the inner secondary wall made up of three different layers - S_1, S_2 and S_3. The hollow interior of the fiber is lumen. The middle lamella surrounds the individual fibers and consists mainly of lignin, Figure 2.2. The cellulose polymer chains form the elementary fibrils which associate to give the fibrillar structure of varying orientation across the different lamellae of the three secondary wall layers. Cellulose occurs predominantly in the S_2 layers. The maximum concentration of lignin occurs in the middle lamella and decreases sharply across the secondary wall layers towards the lumen. In addition to the fibers, hardwoods also have a large number of vessel elements - short, wide, thin walled cells of varying cross sections, developed in the growing tree for sap conduction. Vessels are absent in softwoods and pits consisting of thin perforated membranes interconnect the lumina of the softwood tracheids.

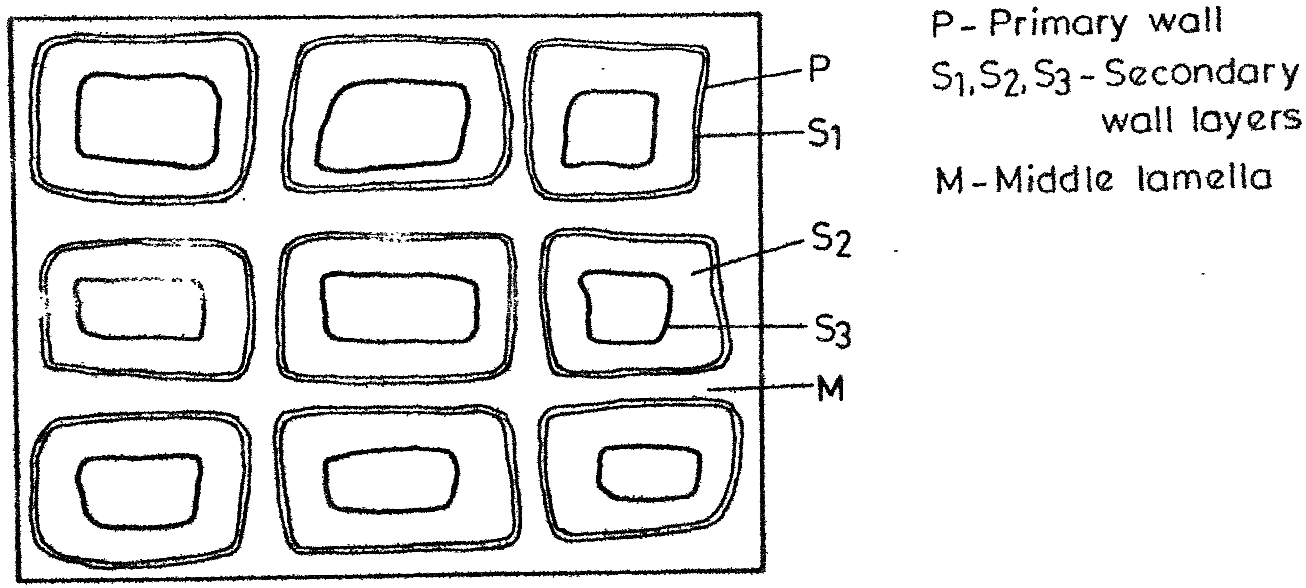


Fig. 2.1 - Cross section of wood fibres showing cell wall layers.

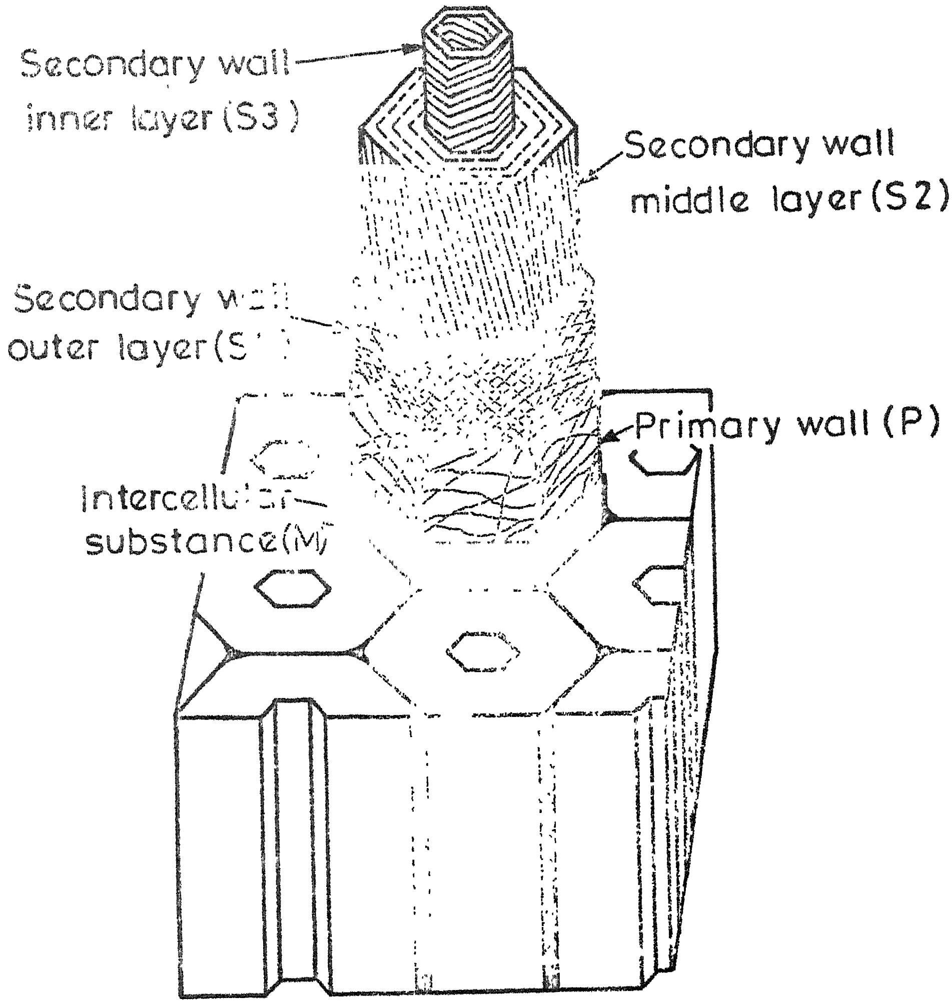


Fig. 2·2 -Cell wall layers of a softwood tracheid or
a hardwood fiber.

It is necessary to selectively remove the lignin substance from the compound middle lamella region to liberate the individual fibers. This can be accomplished by the chemical degradation of the polymeric lignin. Temperature and alkali concentrations used in commercial kraft pulping break down the macromolecular lignin to give simple alkali soluble polymeric fragments. The delignification reactions can progress satisfactorily during kraft pulping with the uniform distribution of the pulping chemicals across the wood chips. Pulping liquor initially reaches the reaction sites in the chip interior mainly by bulk penetration induced by capillary and hydrostatic forces. Subsequent reactions proceed with the diffusion of the pulping species through the moist chips to the active sites. Swelling of the chips in alkaline medium facilitates penetration and diffusion of the pulping chemicals.

During kraft pulping, wood chips are treated with white liquor at 160-180°C for 2-4 hours and the yield of unbleached pulp is 45-54 per cent. Kraft pulping is not selective for delignification reactions and the polysaccharides also undergo partial degradation during the digestion. Sodium sulfide in white liquor hydrolyzes to form sodium hydrosulfide. The pulping reactions involve OH^-, $S^=$ and SH^- ions and the wood constituents. The latter includes several functional groups/linkages in its constituent compounds. Lignin

macromolecule has alcoholic and phenolic hydroxyls, aryl-aryl and alkyl-aryl ethers, benzyl-alcohol ethers, carbonyls, methoxyl, and several other characteristic linkages and reactive groups. The D-glucose units of cellulose are linked together by 1-4-β-glucosidic bonds. The anhydroglucose units of cellulose have primary and secondary alcoholic hydroxyl groups. Cellulose polymer has a reducing end group and a non-reducing end group at the chain ends. Hemicelluloses also have similar structural features and in addition have acetyl and uronic acid substituents. Thus the kraft system consists of a complex wood substance and OH^-, $S^=$ and SH^- ions in the white liquor. All the reactions of wood constituents involve hydroxyl ions; the sulfide/hydrosulfide ions play a significant catalytic role in delignification reactions. (Demethylation reactions of lignin by $S^=$ or SH^- contribute to the odour problem of kraft pulp mills).

Alkali in white liquor causes widespread cleavage of the ether bonds in the lignin macromolecule. Aryl-glycerol-β-aryl ether structure which occurs frequently in many native lignins are the most susceptible to alkaline cleavage reaction. Phenolic -aryl ethers are also hydrolyzed by alkali. Cleavage of the aryl-ether bond increases the proportion of free phenolic groups in the lignin fragments and this facilitates further breakdown of the ether links of the aryl ethers, initially devoid of free phenolic hydroxyl groups. The

nucleophilic hydrosulfide ions in white liquor catalyse the cleavage of the ether bonds in phenolic units and generate additional free phenolic units for further fragmentation of lignin. It also reduces the condensation reactions which can occur in alkaline media forming stable carbon-carbon bonds, such as 5-5', $\alpha - \alpha'$ and $5 - \alpha'$ linkages. Alkaline hydrolysis also breaks the lignin-carbohydrate bonds. Lignin reactions consume about one-fourth of the total alkali consumption of a kraft cook.

Degradation of carbohydrates in alkali occurs through peeling and stopping reactions and random hydrolytic cleavage of the glucosidic bonds. The reducing end groups of cellulose will be peeled off one by one liberating isosaccharinic acids. This peeling process continues until the formation of a stable metasaccharinic acid end unit in the chain by stopping reactions. Random cleavage of glucosidic bonds shortens the chain length and provides additional endgroups for the peeling process. Similar sequence of peeling, stopping and hydrolytic cleavage reactions would also take place with the hemicellulose components. Low molecular weight carbohydrates especially some hemicellulose components will dissolve in alkali. About 50-60 per cent of the alkali added is consumed in these reactions to form the sodium salts of the carbohydrate degradation products.

Volatile extraneous components like terpenes leave the system with the digester relief gases. Resin and fatty

acids are solubilized as soaps in white liquor. Tannin like materials typical of eucalypts, are hydrolyzed with subsequent oxidation and probable condensation with some of the organic constituents of the system. The kraft system thus consists of a complex set of simultaneous reactions and are not easily represented by stoichiometric expressions.

Unbleached kraft pulp generally consists of 65-75 per cent cellulose, 15-25 per cent hemicellulose and 5-10 per cent of residual lignin. The progress of the kraft pulping reactions is represented by the residual lignin content of the pulp produced. Lignin content of the pulp is usually reported as Klason lignin - the residue obtained on hydrolyzing a pulp sample with 72 per cent H_2SO_4. However, for routine chemical analysis an indirect estimate of pulp lignin content is based on oxidation with potassium permanganate. Kappa number is determined by TAPPI standards procedure (T236 os-76) and is equal to the amount (ml) of 0.1N $KMnO_4$ solution consumed by one gram of moisture free sample. Kappa number is widely adopted in both commercial practice and laboratory investigations as an index of the lignin content of the pulp. The usual range of Kappa number is 35-65 and 25-35 for unbleached and bleached grades of softwood paper pulps; the corresponding range for hardwood paper pulps is 20-90 and 15-35 for unbleached and bleached grades.

Kraft pulp also contains a small amount of uncooked or undefibered wood chips and is separated by screening. The screening rejects are recycled for pulping and the screened pulp goes to bleaching and/or paper making. Kraft digester operating conditions are selected to give the maximum screened pulp yield with the desired kappa number.

2.2 Pulp Strength Properties:

The paper web is formed as a uniform network of intermingled fibers by dewatering a dilute suspension of the pulp on a moving band of endless fine wiremesh screen. The residual water is removed in presses and dryers to give paper. Standardized test procedures give the strength properties of the pulp handsheets represented by bursting strength, tearing resistance, tensile strength and folding endurance. These properties are influenced by fiber morphology, pulp type, and the degree of beating and refining during stock preparation for paper making. Reduction in lignin content of the pulp improves flexibility of the fibers to increase the interfiber bonding strengths. Strength properties of the various pulp types increase in the order - mechanical, semichemical and chemical according to their reduced lignin content. The degree of delignification and hemicellulose retention are largely dependent upon active alkali charge, pulping temperature and white liquor sulfidity. Retention of hemicellulose and reduced lignin content in the pulp also improve swelling

and bonding ability of fibers. Degradation of cellulose during pulping lowers bursting and tensile strengths. Beating or refining of the pulp during stock preparation causes fibrillation of the fibers thereby facilitating increased fiber contacts to give improved interfiber bonding strength during the formation of the paper web.

The important morphological properties of fibers include - fiber length, diameter, length-to-diameter ratio and cell wall thickness. The average dimensions of softwood and hardwood pulp fibers are given below.

Dimension	Softwood	Hardwood
length, mm	3 - 5	0.7 - 2
diameter, μm	20 - 40	10 - 30
wall thickness, μm	2 - 5	1 - 8

The long fibers of softwood kraft pulps give superior tearing strength and folding endurance while the short fibers of hardwood kraft pulps give good formation and smooth surface to the paper. Both the softwood and hardwood pulps have comparable bursting and tensile strengths. Fibers with thin walls collapse easily into flat ribbons during pulp stock preparation and paper making to give a better bonding to form dense sheets and improve surface smoothness, whereas fibers with thick cell walls give bulky sheets with an open porous structure. Conservation of the available fiber resources should be possible by an optimum blend of softwood

and hardwood kraft pulps to give a paper of the desired strength properties incorporating the superior qualities of both the long and short fiber pulps.

2.3 Kraft Pulping Variables:

Pulping variables can be considered under two broad categories relating to the available fiber resource and digester operating conditions. The former includes wood species influencing chemical composition and fiber morphology, age, wood density and other geographical growth factors. The important digester output variables are yield, screening rejects, residual lignin content (Kappa number) and strength properties of the pulp. Digester operating variables include - chemical charge, sulfidity (white liquor), temperature, heating period to the desired temperature, pulping time, liquor-to-wood ratio and chip size.

Published literature pertaining to the study of the effects of various factors that influence the kraft pulping process are summarized in several reviews and monographs (Wilder and Daleski, 1964; Rydholm, 1965; Kleppe, 1970). These investigations deal in general with the effect of various factors on yield, Kappa number, and the other pulp properties of several softwoods and some hardwoods of temperate zones. The temperate zone softwoods have higher lignin content compared to the hardwoods. The lignin content of tropical hardwoods is comparable to the temperate zone

softwoods; the macromolecular structure of native lignin of these species also would vary due to differences in the phenyl-propanoid precursors of lignin biosynthesis. Adoption of the pulping conditions recommended for temperate zone woods may not give the desired pulp quality using tropical hardwoods. Differences in chemical composition and distribution of the cell wall constituents would require modified pulping conditions to get equivalent pulp properties. However, for a given wood species, the pulping variables may be expected to have similar influences on yield, Kappa number and other properties of the pulp. A summary of the general range of pulping variables for commercial batch kraft digester operation is given in Table 2.1.

All the operating variables of the kraft digestion process have a strong influence on pulp quality and properties. The latter are also influenced by significant interaction among the pulping variables. Nevertheless, pulping results are observed to show the following general trends of the effects of the different variables.

1. An increase in chemical charge accelerates delignification reactions to reduce Kappa number and yield of the pulp.
2. Digester heating period is selected to provide sufficient time for the uniform impregnation of the chips with white liquor;

TABLE 2.1: GENERAL RANGE OF BATCH KRAFT DIGESTER VARIABLES

Variable	Range	
INPUT VARIABLES		
Chemical charge (% as Na_2O)	12 - 20	
Temperature, °C	160 - 180	
Sulfidity, %	10 - 40	
Liquor:wood	3:1 - 6:1	
Time-to-temperature, min.	60 - 120	
Time-at-temperature, min.	60 - 180	
Chip size, mm		
length	15 - 25	
width	10 - 15	
thickness	2 - 5	
OUTPUT VARIABLES		
Kappa number	15 - 100	
Pulp yield	45 - 55	
Strength properties	Softwoods	Hardwoods
Burst index, (kPa m^2/g)	6 - 12	3 - 8
Tear index, (mN m^2/g)	6 - 25	5 - 12
Tensile index, (N m/g)	50 - 160	45 - 115
Double folds	200 - 3000	30 - 600

it depends mainly upon the thickness and density of the chips.

3. Pulping temperature and time have a reciprocal relationship - a higher temperature requiring reduced pulping time and vice versa. Time-temperature interactions cumulatively representing the digester schedule are represented by the H-factor, based on relative rates of delignification. A rise in temperature or pulping time decreases both pulp yield and Kappa number.
4. An increase in sulfidity of white liquor accelerates delignification reactions to give a lower Kappa number pulp, decreases screen rejects, and improves the strength properties.
5. The concentration of the active pulping chemicals depends upon the liquor:wood ratio; selection of the latter depends upon the digester heating arrangement (open steam or external heat exchanger) and heat load to the black liquor evaporation plant besides proper chip impregnation.
6. The critical chip dimension is the thickness of the chips, controlling the rate of diffusion of OH^-, SH^-

and $S^=$ ions for the replenishment of the reactants in the chip interior for uniform digestion.

A model for the kraft digester should adequately represent the above trends of the effects of the different variables and also include the interaction effects among the pulping variables.

2.4 Kinetics of Delignification Reactions:

A fundamental study of the kinetics of alkaline pulping reactions was first done by Larocque and Maass (1941). Since then several investigations of the rate of delignification reactions have been reported for extractive-free wood meal and wood shavings (1-2 mm) of softwood species (Enkvist et al., 1957; Gierer et al., 1964; Kulkarni and Nolan, 1955; Kleinert, 1966; Caroll, 1960; Wilder and Daleski, 1964; Lemon and Teder, 1973; Edwards et al., 1974; Kerr, 1970). Wilder and Daleski have reviewed the literature on kraft pulping kinetics. The complexity of the kraft system was discussed earlier (section 2.1). The kraft digestion process is essentially a heterogeneous solid-liquid reaction system involving mass transfer and chemical reactions. The overall reaction rate is determined by the following physico-chemical steps in the process:

1. Diffusion of active pulping chemicals (OH^-, SH^- and $S^=$) from white liquor into chips,

2. Adsorption of active pulping species on reaction site in chip interior.

3(a). Delignification reactions - breakdown of the lignin polymer,

(b). Carbohydrate degradation reactions - peeling, hydrolytic cleavage and stopping reactions,

4. Desorption and dissolution of reaction products as sodium salts of polymeric lignin and degraded polysaccharide constituents, and

5. Diffusion of the dissolved wood substances into the spent liquor.

The influence of diffusional resistances to mass transfer can be reduced by using wood meals or thin wood shavings and constant liquor composition (Large liquor-to-wood ratio). With the above conditions the behaviour of the system is approximately described by a pseudohomogeneous model for the bulk delignification phase representing the removal of about 75 per cent of the total lignin.

Equations (2.1) and (2.2) represent the two probable kinetic rate expressions for delignification reactions based on the findings of various investigators.

$$-\frac{dL}{dt} = k_1 L\,[OH^-] + k_2\, L\,[OH^-]^{0.5}\ [S^=]^{\,n} \qquad (2.1)$$

$$- \frac{dL}{dt} = k_3 L \quad [OH^-]_e \tag{2.2}$$

where k_1 - rate constant for delignification associated with hydroxide

k_2 - rate constant for delignification associated with sulfide

k_3 - rate constant for delignification associated with both hydroxide and sulfide

L - residual lignin in the pulp

$[OH^-]$, $[S^=]$ - concentrations of hydroxide and sulfide in white liquor.

$[OH^-]_e$ - concentration of effective alkali in white liquor

n - exponent of sulfide concentration ($n=0.4-0.7$)

Equations (2.1) and (2.2) have given satisfactory fit of the experimental data for softwood species such as pine, spruce, and western hemlock. Equation (2.1) represents the additive effect of delignification caused by hydroxide and the catalytic role of the sulfide ion. Since $S^=$ or SH^- ion plays only a catalytic role in delignification and is not consumed during pulping reactions, equation(2.2) based on the use of effective alkali concentration also represents bulk delignification kinetics. Mass transfer effects would play a significant role in commercial pulping processes and equations describing bulk delignification alone would be

inadequate. The various kinetic studies also do not consider the kinetics of polysaccharide degradation reactions, responsible for the consumption of more than half of the alkali added to the digester. Even though delignification kinetic studies have lead to an understanding of the rate of the overall pulping process, a detailed mechanistic study should include the contributions of all the five major physicochemical steps listed earlier. Inspite of these limitations equation (2.2) has been adopted recentl_ to develop process control strategies for commercial batch kraft digester operation based on measurement of effective alkali concentrations and H-factor to obtain the desired pulp Kappa number (Chari, 1973; Wallin and Noreus, 1973; Wells et al., 1975; Kerr, 1976).

2.5 Models for Kraft Pulping:

The complexity of kraft system and the lack of satisfactory mechanistic kinetic models has necessitated the development of empirical models to correlate pulp properties with digester variables. These models represent the overall kraft pulping process and are satisfactory for the selection of pulping conditions necessary to achieve the desired pulp qualities.

The empirical models give the functional relationship between the observed responses (pulp properties) and process (digester) variables and can be used for determining the

optimum pulping conditions within the experimental region. Such representations are also useful for process control.

A summary of empirical kraft pulping models is given in Table 2.2. Among the earlier investigations on this topic, Hatton et al.(1972) have proposed simple linear model relating pulp yield to permanganate number or Kappa number for softwood species [model 1]. The values of the constants in the model depend upon wood species and the range of pulping conditions. Luzina (1966) has correlated experimental pulp yield data with active alkali, temperature and time [model 2]. Hatton et al. (1972, 1973) have correlated kraft pulp yield of western hemlock and trembling aspen with effective alkali and H-factor [models 3 and 4]. A Finnish mill has obtained a second order regression equation [5] relating Kappa number with active alkali and H-factor. Hatton (1972) also has correlated yield to effective alkali and H-factor by a second order equation including linear and interaction terms [6].

Hinrichs (1967) developed a cubic regression equation assuming no interaction terms, relating the six independent variables - effective alkali, percent sulfide, temperature, liquor-to-wood ratio, cooking time and chip length to dependent output variables for the pulping of Douglas fir chips [7]. Later models are based mostly on regression approaches, in which digester output responses have been correlated with the digester input variables by a general second order model.

TABLE 2.2: SUMMARY OF EMPIRICAL MODELS FOR KRAFT PULPING

Model No.	Author(s)	Species	Model Equation	Remarks
1.	Hatton et al.(1972)	Softwoods	$Y = b_1 + b_2 K$	b_1, b_2 constants
2.	Luzina (1966)	Pine	$Y = b_1(\frac{X_1}{10})^{-b_2 X_2^{0.7} X_5^{0.4}}$	
3.	Hatton et al.(1972)	Hemlock	$(Y_t - b_1 \exp(X_1' - b_2)^{-1})\ X_1'\ H = b_3$	good agreement
4.	Hatton and Hejjas (1973)	Aspen	$(Y_t - b_1 \exp((X_1' - b_2) + \frac{X_1'}{b_3})^{-1})\ X_1'\ H = b_4$	$b_1 - b_4$ constant
5.	Kleppe (1970)	For a Finnish mill(1967)	$K = b_o - b_1 X_1 + b_2 X_1^2 - b_3 H + b_4 X_1 H$	Kappa no. 26-45 X_1 16-18
6.	Hatton (1972)	Softwood	$Y = b_o + b_1 X_1' + b_2 X_1'^2 + b_3 H + b_4 H^2 + b_5 X_1' H$	
7.	Hinrichs (1967)	Douglas fir	$y = b_o + \sum_1^k b_i x_i + \sum_1^k b_{ii} x_i^2 + \sum_1^k b_{iii} x_i^3$	
8.	Bailey et al(1969) Garceau et al.(1974) Chen et al.(1974) Mathur & Peterson (1978)	Pine Pine Pine Pine	$y = b_o + \sum_1^k b_i x_i + \sum_1^k b_{ii} x_i^2 + \sum_{i<j}^k b_{ij} x_i x_j$	$R^2 = 0.66 - 0.87$
9.	Wallin & Noreus (1973)	Pine & birch	$\frac{1}{H} = \sum_{i=0}^{n} \sum_{j=0}^{m} b_{ij} (X_1')^i (K)^j$	

Table 2.2 (contd)

Model No.	Author(s)	Species	Model Equation	Remarks
10.	Hatton (1973)	Softwood/ hardwood	$Y, P \text{ or } K = b_o - b_1(\log(H)\ (x_1')^n)$	$n = 0.35$ (softwoods)
11.	Hatton (1976)	"	$Y, P \text{ or } K = b_o - b_1(\log(H)(x_1')^n) + b_2(\log(H)\ (x_1')^n)^2$	$n = 0.76 - 1.35$ (hardwoods) $R^2 = 0.7 - 0.8$
12.	Lodzinski & Karlsson (1976)	"	$\frac{1}{Y} \text{ or } \frac{1}{K} = b_o + b_1(\log(H)\ (x_1')^n)$	
13.	Edwards & Noreberg (1973)	"	$(Y\ K) = b_1 \frac{(X_4)^{n_4}}{(X_1)^{n_1}\ (H)^{n_9}}$	
14.	Chari (1973) Lin et al.(1978)	Softwoods Hardwoods	$P \text{ or } K = b_1 \frac{(X_4)^{n_4}}{(X_1)^{n_1}\ (H)^{n_9}}$	b_1=1835-3976 for seven hardwoods

One of the chief advantages of this model is that very satisfactory correlations can be developed from statistically designed experimental designs. Bailey et al. (1969) have correlated yield, Kappa number and strength properties data by model [8] using a second-order central composite rotatable experimental design with 5 variables. The model was also adopted for mill batch digester trials and it was shown that 66-87 per cent of the variations are accounted for by the model (McKibbins et al., 1970). Models of the form [8] have also been used by Garceau et al. (1974); Chen et al. (1974), and Mathur and Peterson (1978) for correlating laboratory pulping data.

The linear regression model involving five or six pulping variables, model [8] , although very useful and satisfactory, needs a large number of parameters to be estimated. Simpler models are obtained by the use of H-factor, which expresses the combined effect of three pulping variables - heating period, temperature and pulping time. Wallin and Noreus (1973) have obtained a model correlating effective alkali, H-factor, and Kappa number and developed a process control system to obtain pulps of desired Kappa number based on measurement of effective alkali concentration [9].

Hatton (1973, 1976) has correlated yield, permanganate number and Kappa number data for the pulping of softwoods and hardwoods with H-factor and effective alkali [model 10]; the

value of the exponent n was essentially constant (n = 0.35 - 0.41) for softwoods (Alpine fir, Balsam fir, Douglas fir, western hemlock, jack pine and red cedar) and varied (n = 0.76 - 1.35) for hardwoods (beech, hard maple, red alder, yellow birch and trembling aspen). Later, Hatton (1976) has reported a slight improvement in the model by the inclusion of a quadratic term in the above model [11]. Lodzinski and Karlsson (1976) have correlated H-factor and effective alkali with the reciprocal of yield or Kappa number [12].

Non-linear models [13, 14] have also been proposed involving chemical charge (active alkali), H-factor and liquor-to-wood ratio. Edwards and Norberg (1973) obtained good correlation of these variables with the product of yield and Kappa number [13]. The model proposed by Chari (1973) also correlated these three variables with permanganate number [14]. This model was implemented for the computer control of mill batch digester to improve pulp yield and uniformity. Lin et al. (1978) have developed a similar model [14] for the prediction of Kappa number of several hardwood kraft pulps and the specific constant (b_1) varied with the species (b_1 = 1835 - 3976 for seven hardwood species).

Several of the above models have been developed for routine pulp mill control operating at a constant sulfidity and liquor :wood ratio levels and consequently these are not included as variables in the model. They are directly

useful for the control of yield (uniformity), permanganate number/Kappa number for the particular species and are applicable for the range of pulping conditions used in developing the models. The general second-order model [8] takes into account all the important pulping variables and can be used to represent most of the digester responses with satisfactory correlation and is used in this study.

CHAPTER 3

METHODOLOGY FOR MODEL DEVELOPMENT AND OPTIMIZATION

A process model is the mathematical representation of the actual process. Rigorous model of a chemical process requires a knowledge of the principal governing mechanisms and a precise estimation of the model parameters. A theoretical/mechanistic model can be developed easily for a simple process from physico-chemical principles of the related transport phenomena occurring in the process. However, the mechanisms underlying the overall pulping process are complex though plausible reaction mechanisms and kinetic models have been proposed for delignification and carbohydrate degradation reactions based on studies with model compounds and isolated constituents of wood. Empirical models are usually proposed for kraft pulping to enable a meaningful interpretation of the observed effects. An empirical model represents the functional relationship between the observed response and the range of process variables considered.

A comprehensive empirical model can be developed by considering all the independent variables (factors) over the range of interest using appropriate statistical experimental designs; such an approach will be satisfactory for systems of known behaviour. Alternatively, a sequential model building approach will be suitable for an entirely new process or for a system with less a'priori information. The model will be

developed iteratively to assess the relative contributions of the factors to the observed response based on the results of simple exploratory experimental designs of selected variables. Such an approach will also facilitate location of the desired range of the experimental variables. The final model will incorporate the effects of all the pertinent variables. The above procedures based on experimental designs require fewer experiments and are superior to the conventional trial and error techniques or methods based on the study of the influence of a single variable at selected fixed conditions for the other variables. Response surface methods have been developed based on sequential model building approach to (1) represent the functional interrelationship between the input variables of the system and one or more of the observed responses, (2) to select operating conditions to give the desired response(s), (3) to locate the optimum operating conditions, and (4) to graphically represent the effects of the different input variables about the optimum operating conditions as well as by two-dimensional contour plots for the response with two most important pulping variables.

3.1 Experimental Designs:

Several experimental designs are available for selecting the appropriate range of experimental conditions and to determine the nature of response surface. The number of experiments and the design pattern selected will depend upon the functional

relationship between the response and the various input variables. A simple linear relationship between the response (y) and a single variable (x) will require only two sets of data for representation. With two or more variables factorial experimental designs are more suitable for response surface studies. In a factorial experiment the effects of a selected number of independent variables are investigated simultaneously using specific combinations of the factors at 2 or 3 (usually) levels for each variable. A factorial design for k variables at $l_1, l_2, \ldots l_k$ levels of each variable will require $l_1 \times l_2 \times \ldots\ldots \times l_k$ number of experiments; the selection of the factors at two levels is adequate in most instances to determine the main and interaction effects besides reducing the number of experiments at each stage of sequential experimentation. Additional experiments can be added to the factorial design to form composite designs for a detailed study. With four or more independent variables, fractional factorial and composite designs reduce the number of experiments. A three level factorial design (3^k) can account for quadratic effect of the factors and require a large number of experiments; the desired quadratic effect can also be obtained with a central composite design augumenting the two-level (fractional) factorial design.

The following experimental designs are adopted in this

investigation dealing with pulping of eucalypt, pine and binary (eucalypt + pine) chip blends:

(a) 2-level 2-factor designs (4 experiments),

(b) 2-level 3-factor designs (8 experiments),

(c) 3 x 2 (2-factor) design (6 experiments),

(d) fractional factorial design for five factors (16 experiments), and

(e) central composite rotatable design for five factors (32 experiments).

The sequence of experimentation using the above designs for studying the kraft pulping behaviour of eucalypt and pine chips is discussed next.

3.2 Designs for Pulping Experiments:

Process variables of the kraft system include chemical charge (active alkali), sulfidity, time-to-maximum cooking temperature, maximum cooking temperature, time of cooling at maximum temperature, liquor-to-wood ratio and chip size. The proportion of pine and eucalypt chips will be an additional variable for the experiments using binary chip blends. A comprehensive two-level factorial design for the kraft system would require 128 (2^7) experiments and can be reduced by decreasing the number of variables. The heating period required to raise the digester contents to pulping temperature is an important pulping variable interacting with pulping temperature and govern the uniform impregnation of the chips

with pulping liquor to ensure low screening rejects in the pulp. The effect of these two variables on screened pulp yield can be studied using a 2-level 2-factor design and a constant heating period with minimum screening rejects selected for all the subsequent experiments. Commercial pulp production uses mill run chips with a fairly wide size distribution since the mill screening system separates only the large/oversize fraction. It would be desirable to study the influence of chip size (thickness) on pulping behaviour using simple experimental designs and fractionated chips. The dominant chip size fraction can be used for all the pulping experiments. The selection of a constant heating period and the dominant chip size would result in five kraft pulping variables requiring only 32 (2^5) experiments for a two-level factorial design and 16 experiments for a half replicate fractional factorial design. Both the above designs can be made rotatable designs by additional (2k) experiments at the star points to ensure that the estimated response has a constant variance at all points equidistant from the center of the design. The coded value of the variable for star points (α) is given by ($2^{k/4}$) for a full factorial design and ($2^{(k-1)/4}$) for a half replicate of fractional factorial design. The further addition of 6 replicate experiments at the central point conditions will give an estimate of the experimental error and the complete design is termed as

central - composite rotatable design. The representation of independent variables of a 2-level factorial design is facilitated by adopting the following general code, equation (3.1), to give a value of +1 and -1 corresponding to the upper and lower levels of the coded variables.

$$x_i = \frac{X_i - X_{io}}{V_i} \qquad (3.1)$$

where x_i - coded value of the ith variable (factor),

X_i - actual value of the ith variable

X_{io} - actual value of the ith variable at central point

V_i - half the range of ith variable.

Combinations of the selected variables represented by their coded values form the design matrix for the experiments. A summary of the various experimental designs used in this study for the pulping of eucalypt, pine and binary chip blends is given in Table 3.1. Typical design matrices for a 2-level -3factor, (2^3 factorial), 3 x 2 factorial and central-composite rotatable experimental designs are given in Tables 3.2, 3.3 and 3.4 respectively. Figure 3.1 is a geometrical representation of a 2-level 3-factor experimental design in a 3-dimensional space.

3.3 Analysis of Experimental Data:

Data obtained from the factorial experimental designs can be used to estimate the main effects of the factors on the observed response and also the degree of interaction amongst

TABLE 3.1: EXPERIMENTAL DESIGN SELECTED FOR THE KRAFT PULPING OF EUCALYPT, PINE AND BINARY CHIP BLENDS

S.No.	Pulping variables	No. of variables (factors)	Design	No. of experiments
		A. EUCALYPT		
ED-1	Temperature (x_2) Time-to-temperature (x_7)	2	factorial (2-level)	4
ED-2	Chemical charge (x_1) Chip size (x_6)	2	factorial (3x2)	6
ED-3	Chemical charge (x_1) Temperature (x_2) Sulfidity (x_3) Liquor-to-wood ratio (x_4) Time (x_5)	5	a. Fractional factorial b. Second order central composite rotatable design	16 32
		B. PINE		
ED-4	Chemical charge (x_1) Temperature (x_2) Time (x_5)	3	factorial (2-level)	8
ED-5	Temperature (x_2) Time-to-temperature (x_7)	2	factorial (2-level)	4
ED-6	Chemical charge (x_1) Temperature (x_2) Chip size (x_6)	3	factorial (2-level)	8
ED-7	Chemical charge (x_1) Temperature (x_2) Sulfidity (x_3) Liquor-to-wood ratio (x_4) Time (x_5)	5	½ replicate of a 2-level fractional factorial design and six replicates	22
		C. BINARY CHIP BLENDS		
ED-8	Chemical charge (x_1) Temperature (x_2) Pine fraction (x_8)	3	factorial (2-level)	8

TABLE 3.2: DESIGN MATRIX
2^3 FACTORIAL DESIGN

Run No.	Design matrix variables			Treatment combination
	A	B	C	
1	-1	-1	-1	1
2	+1	-1	-1	a
3	-1	+1	-1	b
4	+1	+1	-1	ab
5	-1	-1	+1	c
6	+1	-1	+1	ac
7	-1	+1	+1	bc
8	+1	+1	+1	abc

Pine - exploratory experiments

A - Chemical charge

B - Temperature

C - Time

TABLE 3.3: DESIGN MATRIX

3x2 FACTORIAL DESIGN

Run No.	Design matrix Variables	
	A (x_1)	B (x_6)
1	-1	-1
2	0	-1
3	+1	-1
4	-1	+1
5	0	+1
6	+1	+1

In the experiments dealing with the influence of chip thicknes (eucalypt) the variables correspond to:

A - Chemical charge

B - Chip thickness

TABLE 3.4: DESIGN MATRIX

Central Composite Second-Order Rotatable Design
(5 Independent Variables)

Run No.	Chemical charge (AA) x_1	Temperature (T) x_2	Sulfidity (S) x_3	Liquor-to-wood ratio (D) x_4	Time (t) x_5
	A. <u>Factorial Design</u>				
1	-1	-1	-1	-1	+1
2	+1	-1	-1	-1	-1
3	-1	+1	-1	-1	-1
4	+1	+1	-1	-1	+1
5	-1	-1	+1	-1	-1
6	+1	-1	+1	-1	+1
7	-1	+1	+1	-1	+1
8	+1	+1	+1	-1	-1
9	-1	-1	-1	+1	-1
10	+1	-1	-1	+1	+1
11	-1	+1	-1	+1	+1
12	+1	+1	-1	+1	-1
13	-1	-1	+1	+1	+1
14	+1	-1	+1	+1	-1
15	-1	+1	+1	+1	-1
16	+1	+1	+1	+1	+1

Table 3.4 (contd)

Run No.	x_1	x_2	x_3	x_4	x_5
	B. Star Points				
17	−2	0	0	0	0
18	+2	0	0	0	0
19	0	−2	0	0	0
20	0	+2	0	0	0
21	0	0	−2	0	0
22	0	0	+2	0	0
23	0	0	0	−2	0
24	0	0	0	+2	0
25	0	0	0	0	−2
26	0	0	0	0	+2
	C. Central Points				
27	0	0	0	0	0
28	0	0	0	0	0
29	0	0	0	0	0
30	0	0	0	0	0
31	0	0	0	0	0
32	0	0	0	0	0

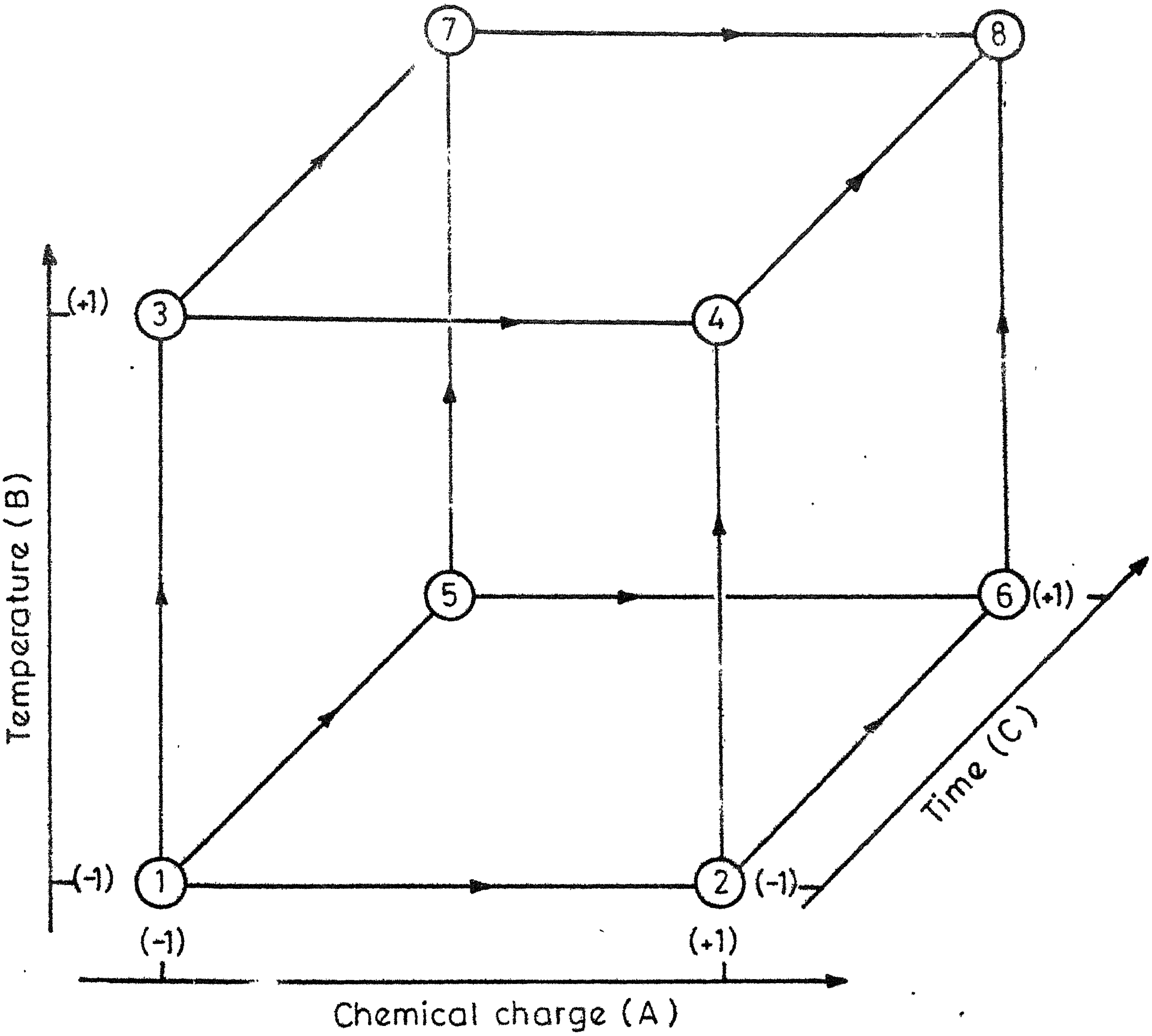


Fig. 3·1 - Geometrical representation of a 2^3 factorial design.

the factors. The main effect of a variable measures the average effect of a change from the low to the high level of that factor over all conditions of the other variables. The interaction effect is observed to be the difference between the average effects of the two factors concerned. For a simple two-level three factor design represented by a cube, the main effects may be considered as a contrast between observations on parallel faces while the interaction depicts the contrast between results on two diagonal planes. The main and interaction effects can be determined from first principles or alternatively by short-cut methods using a table of contrast coefficients or rapidly by the Yates's algorithm (Box et al., 1978).

Experimental data from the factorial designs can also be used to develop mathematical models of the pulping process by response surface methods. A general response surface for the pulping process can be represented by equation (3.2).

$$y_i = f\,(x_{1i}, x_{2i}, \ldots, x_{ki}); \quad i = 1, 2, \ldots, N \quad (3.2)$$

where k and N represent total number of variables and experiments respectively.

The response function in general will have linear, interaction and second order terms of the independent variables together with the unknown coefficients or parameters to be determined from experimental data. These coefficients are

estimated by regression analysis by the least squares method. The sum of squares of the difference between the actual and predicted values of the response represented by the objective function $\underline{S}$ in equation (3.3), is minimized to fit the data to the proposed response relationship. An ideal fit will correspond to $\underline{S} = 0$ (Appendix I).

$$\underline{S} = \sum_{i=1}^{N} (y_i - y_i')^2 \qquad (3.3)$$

where y_i, y_i' - experimental and predicted values of the response respectively

N - total number of experiments.

The adequacy of the model proposed is determined by calculating the multiple correlation coefficient (R^2) defined as the ratio of variation accounted by the model to the total variation. Since all the measurements are subject to experimental error, the estimated coefficients may not be the true coefficients and will have an error variance associated with it. The error variance of the overall model and the experimental error variance (determined from the replicate experiments) give the F-ratio which should be less than the tabulated values of F-ratio at specified degrees of freedom for the model to be adequate. When the error variance associated with each of the estimated coefficients is within the confidence limit of the experimental error variance determined by students 't' test

then the coefficients and the associated variables are considered significant and the remaining terms are deleted. In the subsequent iterative stages of response surface fitting all the statistically significant terms are retained to get the final model. (A detailed procedure of the above analysis is presented in Appendix I).

3.4 Optimization Methods:

The regression models can be used to locate the optimum pulping conditions necessary to give pulp of desired qualities (specifications). The problem of optimization of the response is relatively easy in the absence of constraints. In such cases the model relating input parameters to the output response is differentiated with respect to each x_i in turn and is set equal to zero. The resulting set of simultaneous algebraic equations are solved to obtain the optimum value of $\underline{x}$ that maximizes y. Various optimization techniques are available for use on computer (Beveridge and Schechter, 1970).

However, when the function to be optimized is constrained by other functions and/or boundary conditions (linear or non-linear), the problem of optimization becomes more involved. Sequential search techniques are employed in solving such problems numerically. The principle of sequential search methods consists of the following basic steps:

1. A set of feasible values of the independent variables which satisfy any restriction is

selected as the initial base point.

2. The objective function is evaluated at this base point.
3. A second feasible location is selected (by any appropriate method).
4. The objective function is evaluated at this location.
5. The value of the objective function at this location is compared with that at the base point.
6. If the second point is better, this point is taken as the new base point and the search is continued. If the initial base point was better, the search is continued in an alternative direction.

The different search techniques vary only in step 3. These techniques vary according to the method used to determine the direction and distance of the next search from the base point. Numerical optimization under inequality constraints is a more general type of optimization problem. A number of methods are being developed to solve such constrained problems. All such methods are best suited to specific class of problems. In multivariable constrained problems, the methods differ only in the way in which they find the feasible point and feasible direction (A feasible point is one that satisfies all the

constraints). The methods are divided into two broad classes - gradient and non-gradient. 'Constrained Rosenbrock Method' is a gradient method and 'Complex Method of Box' is a non-gradient method (Rosenbrock, 1960; Box, 1965). Constrained Rosenbrock Method is the most efficient of all the methods available (Box, 1965). The computer programms of these two methods used in this study are given in Appendix IX. (Kuester and Mize, 1973).

Initial feasible points were selected to be the central point pulping conditions. The central point (or base level) conditions are normally selected to be the combination of factors (variable levels) corresponding to the best conditions determined by the analysis of 'a priori' information. Both of the above methods were used and constrained Rosenbrock method was found superior to the Complex Method of Box for the optimization of the pulping process. Experiments were conducted to verify the optimum pulping conditions predicted by Constrained Rosenbrock Method for the desired specifications of pulp properties.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 Wood Chips:

A common lot of eucalypt chips (1000 kg) was collected (Batch 1) from the mill chipper house and screened manually in the laboratory. About one quarter of the sample was collected in the fraction passing through 25 mm and retained on 16 mm (square mesh) screens having an average thickness of 4.4 mm knots, defective/irregular chips and chips above 6 mm thickness were removed by hand sorting and discarded. These chips were stored in polythene bags and used for the experiments dealing with the influence of time-to-temperature (E-1 to E-4, E-1R, E-4R) and the main experiments of second-order central composite rotatable design (E-21 to E-52). Another lot of 150 kg of chips was collected (Batch 2) to get the two fractions (-18 +12 and -12 +6 mm with average thicknesses 3.5 and 2.5 mm respectively) required for the experiments dealing with the influence of chip thickness (E-11 to E-16). One more lot of 80 kg (Batch 4) was screened and -18 +12 mm fraction used for the binary chip blend experiments (E/P/EP-1 to 8). Mill run chips were also used (E-61, E-62) after removing irregular shaped chips hindering digester filling.

A similar procedure was adopted to obtain pine chips in the desired ranges (-25 +18, -18+12 and -12+6 mm

TABLE 4.1: EUCALYPT AND PINE CHIP COLLECTION DATA FOR THE PULPING EXPERIMENTS

	Chip Collection				Experimental Designs	
	Mill chips kg	Fraction: Size range mm	Fraction: Average chip thickness mm	Amount kg	Experiment Nos.	Pulping study
A. Eucalypt						
Batch 1	1000	-25+16	4.4	250	E-1 to E-4 E-1R, E-4R	Effect of time-to-temperature
					E-21 to E-52 E-71 to E-72	Effect of five pulping variables Soda pulping
Batch 2	150	-18+12, -12+6	3.5 2.5	100	E-11 to E-16	Effect of chip size (thickness)
Batch 3	20	Mill run	1.5 - 5.6	20	E-61, E-62	Pulping of mill run chips at normal conditions
Batch 4	80	-18+12	3.5	40	E/P/EP - 1 to 8	Chip blend pulping - three compartment
B. Pine						
Batch 1	100	-25+18	4.7	25	P-1 to P-8	Exploratory experiments
Batch 2	100	-25+18, -18+12, -12+6	4.7 4.0 2.8	50	P-11 to P-14 P-21 to P-28	Effect of time-to-temperature Effect of chip size
Batch 3	500	-18+12	4.0	100	P-31 to P-52	Effect of five pulping variables
Batch 4	30	-18+12	4.0	10	E/P/EP - 1 to 8	Chip blend pulping - three compartment

E/P/EP - Eucalypt, pine and binary chip blends separated in three compartments

TABLE 4.2: COMPOSITION OF TYPICAL MILL WHITE LIQUOR

Compound	Concentration, kg m^{-3} as chemical	as Na_2O
NaOH	84.0	65.1
Na_2S	10.1	8.1
Na_2CO_3	27.2	15.9
Total alkali	89.1	
Active alkali	73.3	
Effective alkali	69.1	
Causticization efficiency,%	80.4	
Activity, %	82.2	
Causticity, %	89.0	
Sulfidity,%	11.0	

discontinued and the digester pressure was relieved in 60 min. to normal atmospheric pressure. The digester temperature decreased to 140°C in 20-25 min. in all the experiments. Subsequently the digester was opened and black liquor was separated by draining and a sample preserved for analysis. The pulp was transferred to a rectangular tray provided with 200 mesh screen and was simultaneously washed and disintegrated manually with continuous supply of water through a hose connection. Dewatered pulp was used for beating and handsheet preparation, and a small aliquot sample used for moisture determination.

Pulps from all the experiments with eucalypt contained very little rejects and did not require a separate screening operation. Experiments (E-37, E-39 and E-1) conducted at lower level of chemical charge, temperature and, time-to-temperature resulted in pulps containing probably upto 2.0 per cent rejects as estimated from the weight of the uncooked chips/hard pulps clusters in the air dry pulp. These pieces probably would not contribute to screen rejects with a mechanical distintegrator. Experimental procedure for the pulping of eucalypt and pine chips were identical. Pulp from pine chips contained a small amount of uncooked chips and hard pulp clusters as rejects and were removed by hand sorting and oven dried to determine screened yield of pulp.

The adjustable compartments in the digester were obtained by two perforated (2 mm holes) stainless steel plates (diam - 19.5 mm) sliding along a central stainless steel pipe (diam - 1.9 cm, length 45 cm) enclosing the digester thermostat probe at the bottom and extending to the top of the digester. The two plates were secured at the desired positions to the central pipe by short stainless steel sleeves at the center with provision for fixing by screws.

The required amount of pine chips (0.15 - 0.45 kg o.d.) was added first and the first plate fixed in position. Eucalypt chips (1.0 - 1.35 kg o.d.) was then added and the second plate secured tight. Blended chips (1.0 - 1.25 kg o.d.) were placed on the top compartment. Pulping was conducted as described earlier. At the conclusion of the cook, the three pulps were collected separately, washed and dewatered. The pulps were treated separately for determination of yield and hand sheet preparation.

4.3 <u>Analysis</u>:

4.3.1 <u>Wood Meal Preparation</u>: Six billets (140 cm long, 7-20 cm diam.) of debarked eucalypt wood were collected (April, 1977) randomly from the wood yard and cut along the length on the saw mill radially/tangentially to form slabs and subsequently cut to form rods and finally cubes (3-4 cm.). The saw dust was collected, air dried and screened on a vibrating sieve shaker to isolate -36+60 mesh fraction (Sample A). Another

collection of ten billets (125 cm long, 5–15 cm diam.) was also subjected to the same treatment to obtain -36+60 and -60 mesh wood meal fractions (Sample B).

Extractive-free wood meal was prepared by the following sequence of treatments: (1) 0.5 per cent NaOH at 98°C and bath ratio of 50:1 for one hour with subsequent washing by hot water, (2) extraction with acetone in a soxhlet apparatus, (3) repeated treatment (thrice) with boiling water for one hr, (4) air drying and storage.

A random collection (April, 1978) of nine logs of debarked pine wood of varying dimensions (30–140 cm long, 5–40 cm diam.) was obtained from the wood yard (These logs consisted of stems and branches of all kind of irregular shapes). Pine wood meal (-36+60 mesh fraction) was obtained by a similar method. Extractive-free pine wood meal was obtained by the following treatments (Tappi standard T12 os-75): Extraction with (a) ethanol-benzene (6 hr), (b) ethanol (one hr) and (c) repeated treatments with boiling water (one hr) and air drying and storage.

4.3.2 <u>Proximate Analysis</u>: Solubility of the original eucalypt wood meal was determined using the following solvents: water (cold, hot), methanol, ethanol, acetone and NaOH (0.5, 1.0 per cent). Pine wood meal was analyzed for its solubility in water (cold, hot), methanol, ethanol-benzene and 1 per cent NaOH. Klason lignin content of both original (only for eucalypt)

and extractive-free wood meal preparations was determined by treatment with 72 per cent H_2SO_4 at 20°C with subsequent dilution and hydrolysis. Holocellulose prepared by repeated treatment (4 times for eucalypt and 6 times for pine) with acidified sodium chlorite was used to determine α-cellulose from solubility in 17.5 per cent NaOH solution at 20°C. Pentosan was determined by treating wood meal with 12 per cent HCl to liberate furfuraldehyde and latter precipitated with phloroglucinol.

4.3.3 Pulp Analysis: The lignin content of pulps was determined as permanganate number (K.no.) and Kappa number using 40 and 100 ml of 0.1N $KMnO_4$ at 30 $\pm$ 3°C by Tappi procedures.

4.3.4 Pulp Fiber Analysis: A sample of air dried pulp (5 g) was dispersed in water by mild agitation with a laboratory stirrer, diluted to a low consistency stained with methylene blue and transferred to microscope slides. With eucalypt pulp, 10 slides were prepared each containing 25-30 fibers. Length and diameter of the individual fibers as well as the diameter of the vessel segments were measured at a magnification of 150 with an optical microscope.

The inter-twined pine pulp fibers on the slides were separated manually (using needles) to prepare 20 slides containing 10-12 fibers each for observation. Length, diameter, wall thickness and lumen diameter were measured at a magnification of 150.

and extractive-free wood meal preparations was determined by treatment with 72 per cent H_2SO_4 at 20°C with subsequent dilution and hydrolysis. Holocellulose prepared by repeated treatment (4 times for eucalypt and 6 times for pine) with acidified sodium chlorite was used to determine α-cellulose from solubility in 17.5 per cent NaOH solution at 20°C. Pentosan was determined by treating wood meal with 12 per cent HCl to liberate furfuraldehyde and latter precipitated with phloroglucinol.

4.3.3 <u>Pulp Analysis</u>: The lignin content of pulps was determined as permanganate number (K.no.) and Kappa number using 40 and 100 ml of 0.1N $KMnO_4$ at 30 ± 3°C by Tappi procedures.

4.3.4 <u>Pulp Fiber Analysis</u>: A sample of air dried pulp (5 g) was dispersed in water by mild agitation with a laboratory stirrer, diluted to a low consistency stained with methylene blue and transferred to microscope slides. With eucalypt pulp, 10 slides were prepared each containing 25-30 fibers. Length and diameter of the individual fibers as well as the diameter of the vessel segments were measured at a magnification of 150 with an optical microscope.

The inter-twined pine pulp fibers on the slides were separated manually (using needles) to prepare 20 slides containing 10-12 fibers each for observation. Length, diameter, wall thickness and lumen diameter were measured at a magnification of 150.

4.3.5 Black Liquor: The concentration of dissolved solids in black liquor sample (10-12 ml) was determined by drying to constant weight in an oven at 105 $\pm$ 1°C. The concentration of residual active alkali was determined by potentiometric titration with 0.1N HCl after eliminating the interfering constituents (lignin and sodium carbonate) by precipitation with 10 per cent $BaCl_2$.

4.4 Handsheet Preparation:

Pulp from each cook was beaten in a laboratory Valley beater (21 liter) at a consistency of 1.6 $\pm$ 0.02 per cent to a final freeness level of 40°SR. Handsheets of 60 $\pm$ 1 gsm basis weight were made in a laboratory sheet maker. Sheets were dewatered with blotting papers by pressing under a couch plate using a couch roll. The sheet was lifted from the wire plate of sheet maker and the blotting paper with the handsheet on it placed on the base of the standard press and subsequently covered with a drying plate. About 20 sheets were prepared in this manner, and the cover plate of the press was subsequently placed on the stack of sheets and bolted. The sheets were pressed at 50 psi (345 kN/m^2) for 5 min. The stack was removed from the press and each plate having a handsheet was fitted into drying rings for air drying of hand sheets. Air dried sheets were removed from the plates and preserved in polythene bags till they were tested.

In three compartment pulping experiments (E/P/EP-series), only eucalypt (E) and chip blend pulps (EP) were beaten to prepare handsheets as the pine pulp (P) was not sufficient for beating.

4.4.1 Strength Properties: Pulp hand sheets were conditioned at 26 $\pm$ 1°C and relative humidity of 70 $\pm$ 5 per cent (for all eucalypt pulp hand sheets). Pine hand sheets were conditioned at 27 $\pm$ 1°C and relative humidity of 75 $\pm$ 5 per cent (P-31 to P-52), 80 per cent (P-11 to P-14) and 82 $\pm$ 2 per cent (P-21 to P-28). Pulp sheets from three-compartment pulping were conditioned at 75 $\pm$ 5 per cent RH. Conditioned hand sheets were used for determination of burst index, tear index, tensile index, stretch and folding endurance. The average of six observations are reported.

CHAPTER 5

RESULTS AND DISCUSSIONS

Kraft pulping behaviour of plantation grown eucalypt and abnormal pine chips are evaluated in this investigation. Plantation grown eucalypt species, popularly known as Mysore gum (hybrid of Eucalyptus tereticornis) is a tropical hardwood grown in Najibabad, Kotdwar, Jawalapur, and Pathri divisions of Uttar Pradesh. It is received by the pulp mill as debarked logs (age = 8-10 years, length = 2m, diameter = 10-20 cm). Mill run chips were observed to be normally regular and relatively free of knots and defects. The proximate chemical composition of eucalypt wood meal is given in Table 5.1 (details are given in Appendix II). The lignin and α-cellulose content are higher compared to temperate zone hardwoods (lignin: 30 vs 22 per cent; α-cellulose: 50 vs 43 per cent). The pentosan content of eucalypt wood meal is determined to be 17 per cent. Optical measurements using well cooked unbeaten kraft pulp samples gave the following average fiber dimensions: length -0.63 mm (s.d. = 0.27 mm), diameter - 0.0089 mm (s.d. = 0.003 mm), and length/diameter ratio - 70. The fiber length and diameter are rather small compared to the normal range for hardwoods (length: 0.7 - 1.5 mm, diameter: 0.015 - 0.025 mm) and may be attributed to the age of this species. The average density of eucalypt chips was determined to be 0.66 gcm^{-3}.

TABLE 5.1: PROXIMATE ANALYSIS OF EUCALYPT WOOD MEAL SAMPLES

Constituents (o.d. basis) per cent	Sample A[a]	Sample B[a]		Guha[f]
	-40+60 mesh	-36+60 mesh	-60 mesh	
<u>Wood meal</u>				
1. Solubilities:				
Water (cold)	-	5.12	2.91	1.8
Water (hot)	4.63	5.79	5.16	13.8
Ethanol	5.12	3.12	3.62	1.11[g]
Methanol	6.24	3.92	4.43	-
1.0 % NaOH	-	12.50	18.33	16.4
0.5 % NaOH[b]	13.27	10.08	16.30	-
Acetone[c]	3.57	3.17	2.07	-
Total extractives[d]	16.36	12.93	18.03	
2. Klason lignin	33.50	35.93	39.05	
<u>Extractive free wood meal</u>				
Klason lignin	23.65	26.59	20.70	(28.3)
	(28.52)[e]	(30.54)	(25.25)	
Holocellulose	58.84	61.07	61.08	(71.0)
	(70.76)	(70.15)	(74.52)	
α-cellulose	41.39	42.72	42.50	(41.7)
	(49.76)	(51.85)	(49.07)	
Pentosans	13.68	14.74	13.09	(15.8)
	(16.45)	(16.90)	(15.97)	
Cross & Bevan cellulose	-	-	-	(53.4)

a Samples A and B collected in April 1976 and April 1978 respectively.
b Extraction conditions: 0.5%, NaOH, 95-98°C, one hour, D=50%
c Extraction of alkali treated wood meal.
d Extraction sequence: 0.5%, NaOH, acetone and water
e Numbers in parenthesis are based on extractive free wood meal
f Reference: Guha (1969) - Mainly 10 years old E.tereticornis
g Alcohol benzene solubility

Standard deviations: Klason lignin (0.59)
Holocellulose (1.29)

The pine (Pinus roxburgii syn. longifolia) used in this work is locally known as twisted chir pine and was obtained from Haldwani, Tehri and Uttar Kashi in Uttar Pradesh, Dharampur (H.P.) and Hoshiarpur (Punjab). Pine wood (age = 70–90 years) available for pulping consisted mainly of abnormal portions of the tree (except stem) left as residuals of forest lumbering operations as irregular shaped branches, stems and knots with varying chemical composition and distribution of lignin and hemicellulose across the primary and secondary wall layers of the fiber and the middle lamella. The proximate analysis of a composite pine wood meal sample given in Table 5.2, showed – lignin = 33.1 per cent, α – cellulose = 46.4 per cent and pentosans = 9.4 per cent. The lignin content is somewhat higher than the normal temperate zone pines (average – 29 per cent). Fiber analysis of the unbeaten kraft pulp samples has shown the following average dimensions: length – 5.0 mm (s.d. = 1.3 mm), diameter – 0.046 mm (s.d. = 0.014 mm), length/diameter ratio – 110, wall thickness – 12.63 μm (s.d. = 2.47 μm) and lumen diameter – 19.81 μm (s.d. = 5.41 μm). The average density of pine chips was determined to be 0.56 gcm^{-3}. The average fiber length and fiber wall thickness are higher than the average values reported for softwoods (average length = 3.5 mm, wall thickness 3–5 μm).

Consequently the pine chips used in this study are heterogeneous in character with an abnormal morphology and

TABLE 5.2: PROXIMATE ANALYSIS OF PINE WOOD MEAL SAMPLES

Constituents, (o.d. basis) per cent	Pinus roxburghii[a]	Pinus khasya[d]	North American Scandinavian pine (range)[e]
Wood meal			
Ash	-	1.70	0.2 - 0.4
Water (cold)	1.73	-	2.2 - 3.3
Water (hot)	5.66	-	1.8 - 4.8
Methanol	5.71	-	-
Ethanol-benzene	6.08	3.44	2.6 - 8.3
1% NaOH q	14.65	12.70	9.9 -19.1
Ethyl ether	-	-	2.0 - 6.8
Total extractives[b]	11.74	-	-
Extractive free wood meal[b]			
Klason lignin	29.22 (33.10)[c]	30.05	25 - 29
Holocellulose	58.72 (66.53)	58.40	68 - 72
α-cellulose	40.92 (46.36)	38.80	44 - 48
Pentosans	8.28 (9.39)	10.34	7.1 - 10.0

a Samples collected in April 1978, Wood meal size: -36+60 mesh
b Extraction sequence: Alcohol-benzene, alcohol and water (Tappi standard T12 os-75)
c Numbers in parenthesis are based on extractive free wood meal
d Reference: Bhaumic and Ghosh (1975)
e Reference: Rydholm (1965); MacDonald (1969).
Standard deviations: Lignin (1.071); Holocellulose (0.633)

chemical composition compared to the temperate zone pine species. Such features would necessitate modified pulping conditions such as chemical charge, temperature, and sulfidity and also affect the pulp properties compared to normal pine chips.

Thus the wood chips used in this work are obtained from (a) reasonably uniform plantation grown eucalypt pulpwood, and (b) abnormal, mature, heterogeneous forest residuals of pinewood. Chip samples were obtained from the chipper line feeding the outside storage piles. Manually screened and hand sorted chips were used for all the experiments of this investigation. Experiments were conducted to obtain unbleached pulps (eucalypt or pine) with Kappa number of 25-60 suitable for making wrapping papers. The development of strength characteristics of unbleached eucalypt and pine kraft pulps were determined for the freeness range of 18-80°SR and it was observed that both the pulp types must be beaten to 40°SR to develop the potential strength properties - tear, burst, tensile and folds (Appendix III).

The results of this investigation are presented and discussed in three sections (5.1, 5.2 and 5.3) dealing with the pulping of eucalypt , pulping of pine, and pulping characteristics of binary (eucalypt-pine) chip blends as outlined below.

Section 5.1: Pulping of Eucalypt

Kraft pulping behaviour of eucalypt chips was studied using three sets of experimental designs.

Set 1: Influence of time-to-temperature and temperature on pulp yield and Kappa number (2-level factorial design, 4 experiments, Expt. Nos. E-1 to E-6).

Set 2: Effect of chip thickness and chemical charge on pulp yield and Kappa number (3x2 factorial design, 6 experiments, Expt.Nos. E-11 to E-16).

Set 3: Influence of chemical charge, temperature, sulfidity, liquor-to-wood ratio and pulping time on pulp yield and quality (fractional factorial design, 16 experiments,Expt. Nos. E-21 to E-36) and (second-order central composite rotatable design, 32 experiments, E-21 to E-52).

Regression equations were developed with the results of above experiments with five independent variables (set 3). These regression models are used to (1) optimize the response function to obtain optimal pulping conditions to achieve the desired pulp yield and quality,(2) graphically depict the effect of each pulping variable on the observed responses while the remaining four variables were held constant at the optimum conditions, and (3) to obtain contour surfaces depicting the combined response of the two important variables -

chemical charge and temperature on yield and properties as a two-dimensional contour plot. The estimated optimum pulping conditions were confirmed experimentally.

Section 5.2: Pulping of Pine:

Kraft pulping of pine chips was also studied in a similar manner with four sets of experimental designs.

Set 1: Exploratory experiments to determine the influence of chemical charge, temperature and time (2-level factorial design, 8 experiments, Expt. Nos. P-1 to P-8).

Set 2: Influence of time-to-temperature and temperature (2-level factorial design, 4 experiments, Expt.Nos. P-11 to P-14).

Set 3: Influence of chip thickness, chemical charge and temperature (2-level factorial design, 8 experiments, Expt.Nos. P-21 toP-28).

Set 4: Influence of chemical charge, temperature, sulfidity, liquor-to-wood ratio and time on pulp yield and quality (half replicate of a 2^5 factorial design plus six replicate runs at the central point conditions, 22 experiments, P-31 to P-52).

Regression equations were developed with the results of the above experiments (set 4). These regression models were used to determine optimum pulping conditions, to graphically

represent the effect of each pulping variable, and to obtain contour plots (2-dimensional) for the combined response of two important pulping variables, similar to the methods adopted for eucalypts. Experiments were conducted at the estimated optimum pulping conditions to check the validity of the models.

Section 5.3: Pulping of Binary Chip Blends:

The ratio of pine/eucalypts becomes an additional variable to be included in evaluating the pulping behaviour of binary chip blends. Models developed for the pulping of eucalypt and pine (sections 5.1 and 5.2) are utilized to estimate the properties of the components of mixed pulps from pulping of binary chips. The properties of composite pulps from chip blends are determined as the weighted average value of the component pulp properties. These estimates are compared with the results from a modified laboratory digester. A 3-compartment digester was used to enable simultaneous pulping of eucalypt, pine and eucalypt-pine chips at constant conditions in three sections separated by perforated partitions to permit uniform liquor distribution. The influence of pine fraction (10-30 per cent), chemical charge and temperature were studied using a 2-level factorial design (8 experiments, E/P/EP-1 to 8).

5.1 KRAFT PULPING OF EUCALYPT

5.1.1 Effect of Time-to-Temperature:

Time-to-temperature represents the heating period to raise the digester contents to the desired pulping temperature. Heating period is an important pulping variable and is interrelated to temperature in determining the uniformity of pulping. The temperature rise period for commercial batch digesters is 60-150 minutes; shorter durations are adequate for continuous digesters with pretreatment of chips by steaming and liquor impregnation.

The effect of time-to-temperature (60, 120 min.) and temperature (160, 170°C) was studied using a simple factorial design and the pulping conditions are given in Table 5.3. The experimental results shown in Table 5.3 are analyzed by Yates's algorithm to determine the main effects and interactions of the two variables.(A sample calculation for the screened pulp yield is given in Appendix V).

Table 5.3 also summarizes the results of Yates's algorithm calculations. The estimates of the effects show that time-to-temperature and pulping temperature significantly influence screened yield while temperature has a dominant effect on Kappa number. An increase in time-to-temperature as well as pulping temperature significantly reduces screen rejects. The interaction effect of the two variables is also observed to have a significant effect on pulp yield. An increase

TABLE 5.3: KRAFT PULPING OF EUCALYPTS: EFFECT OF TIME-TO-TEMPERATURE AND TEMPERATURE

A. Pulping Conditions

Variables	Symbol	Range/Level -1	+1
Time-to-temperature, min.	X_7	60	120
Temperature, °C	X_2	160	170

Constant Pulping Conditions

X_1	Chemical charge (% AA as Na_2O)	16
X_3	Sulfidity, %	21
X_4	Liquor-to-wood ratio	3.6
X_5	Pulping time, min.	60
X_6	Chip size, mm	16-25
	Thickness, mm	4.4
	Standard deviation	1.2

Coding of variables

$x_2 = (X_2 - 165)/5.0 = (-1), (+1)$

$x_7 = (X_7 - 90)/30.0 = (-1), (+1)$

Table 5.3 (contd)

B. Pulping Results

Expt. No.	Pulping conditions t_h min	T °C	Screen rejects %	Pulp yield %	Kappa no.
E-1	60	160	2.7	46.5	31.2
E-2	120	160	1.2	49.0	29.5
E-3	60	170	1.7	46.3	20.2
E-4	120	170	0.6	47.6	22.3
E-1R	60	160	2.4	46.4	33.8
E-4R	120	170	2.8	47.2	24.0

R-Replicate experiments

C. Estimates of Effects by Yates's Algorithm

Effect	Rejects	Pulp yield	Kappa no.
Time-to-temperature (t_h)	-1.25[a]	1.88[a]	-0.2
Temperature (T)	-1.29[a]	0.82[a]	-9.1[a]
Interaction(t_h x T)	0.20	-0.60[a]	1.9
95% confidence interval	±0.85	±0.29	±2.27
Error variance (s_y^2)	1.17	0.04	2.42

a significant at 95% confidence level

in time-to-temperature provides adequate time for the diffusion of pulping reagents into the chip interior and ensures uniform pulping with less screen rejects to improve the yield of screened pulp. Significant interaction effect suggests that it will be advantageous to pulp at a lower temperature and to allow a longer heating period.

Heterogeneity in pulping occurs from gradients in chemical concentration and temperature across the wood chip thickness. The probable mechanism in kraft delignification can be explained by the moving interface theory in which the chemicals are transported through the chips by liquor penetration as well as by diffusion under the influence of a concentration gradient. During the heating period, the temperature of the digester increases gradually, the liquor penetration proceeds fairly slowly and chemicals are consumed in hemicellulose degradation reactions; however, limited delignification occurs until about 140°C (Hartler and Onisko, 1962). Liquor penetration should be complete at the end of the first phase at 140°C, so that diffusion is not hampered during the subsequent delignification step (Borlew and Miller, 1970). During the latter heating period to the desired pulping temperature more than half of lignin is extracted.

With long heating periods penetration is satisfactory for uniform delignification and thus decrease the possibility of uncooked chips (rejects) and improve screened yield of pulp.

However, with short heating periods, delignification will start prior to complete chip impregnation. Heterogeniety in pulping can occur with an increase in temperature because the rate of delignification increases relatively more than the rate of diffusion. The former is approximately doubled upon a 10° increase in temperature, whereas the latter increases only in proportion to the absolute temperature. Thus, both the rapid heating period and high temperature can cause non uniform pulping with an increase in the quantity of rejects (Hartler and Onisko, 1962; Colombo et al, 1964) in batch pulping.

The results of this study show that, by increasing the time-to-temperature from 60 to 120 min. the pulp yield will be 49.0 per cent at 160°C and 47.4 per cent at 170°C. This result is in agreement with the results reported by Stone and Firderreuther (Borlew and Miller, 1970). A constant heating period of 90 min. is selected for all the subsequent experiments of this study.

5.1.2 Influence of Chip Size (Thickness):

The principal dimensions of wood chips consist of length, width and thickness - observed in the longitudinal, tangential and radial directions respectively. The recommended size range of commercial chips is - length (15-25 mm), width (10-15 mm), and thickness (2-5 mm). The chips swell in alkaline medium and the rate of penetration of white liquor

is nearly equal in all the three directions. Borlew and Miller (1970) and Hatton (1978) have discussed the inadequacies of the conventional William's classifier and indicated the need for a modified system to fractionate chips including thickness as an important dimension. Borlew and Miller have recommended an optimum thickness of 3 mm for uniform kraft delignification. Hatton (1978) has summarized the various considerations in chip quality evaluation and compiled a list of the principal chip quality parameters, Table 5.4. However, the majority of these cannot be determined in routine mill control. Steffes (1978) has described a disc screen classifier to remove overthick chips ($>$ 8 mm) and thus eliminate knotter rejects. Recently, Lapointe (1979) has described a chip classifier for a series of thickness and length fractions. Lapointe has reported the best chip thickness of 2-6 mm for batch digestion of hardwoods and 4-10 mm for softwood pulping in Kamyr digesters. The above discussion shows the importance of chip thickness (2-6 mm) as a parameter in determining pulp qualities.

Commercial eucalypt chips were manually screened using wire mesh screens with square openings (25, 18, 12 and 6 mm) to give following chip fractions: -25+18, -18+12 and -12+6 mm with average thicknesses-4.4, 3.5 and 2.5 mm respectively. Unlike other pulping variables, chip size is discontinuous and cannot be selected at the specific values

TABLE 5.4: PRINCIPAL CHIP QUALITY PARAMETERS

	Parameter	Routine measurement
1.	Average moisture content	P
2.	Range of moisture content	DI
3.	Bulk density	P
4.	Chip size fractions	P
5.	Chip length	D
6.	Chip width	PD
7.	Chip thickness	PD
8.	Diagonal: thickness ratio	D
9.	Compression damage	D
10.	Chip contaminants	
	- bark	PD
	- knot wood	P
	- leaves/needles	D
	- extraneous dirt	D
	- internal inorganics	D
	- decayed wood	D
11.	Species identification	D
12.	Ratio of species in mix	D
13.	Sapwood:heartwood ratio	I
14.	Sawmill: woodroom chip ratio	I

P = Practical, D = difficult, I = impossible

Reference: Hatton (1978)

required by the factorial experimental designs. In actual mill practice, chips have a wide range of sizes. Hence the variations in chip size can be reduced by manual screening and hand sorting for research purposes. The mill run chips were regular and had straight grains with uniform thickness and free from knots and defective/irregular chips. It was observed that the length (5-35 mm) and thickness (1.5 - 6.0 mm) of the chips were in the desired range.

Chip thickness and chemical charge are selected as the two variables to ensure uniform liquor impregnation for satisfactory pulping. Six experiments were conducted by 3x2 factorial design with two chip fractions (chip thickness: 2.5 and 3.5 mm) and chemical charge of 15, 16 and 17 per cent active alkali. Table 5.5 shows the range of the pulping variables and other constant conditions. The pulping conditions, experimental results and data analysis by Yates's algorithm (Appendix VI) are summarized in Table 5.6.

Chemical charge has a pronounced effect on pulp yield and Kappa number compared to chip thickness. The strong influence of chemical charge can be seen from the presence of higher quadratic effects in Yates's analysis. Results show that for a given chip size fraction, an increase in chemical charge lowers the pulp yield and Kappa number. Chemical charge exhibits a positive quadratic effect on pulp yield and has a negative influence on Kappa number - a lower level of

TABLE 5.5: INFLUENCE OF CHEMICAL CHARGE AND CHIP SIZE ON THE KRAFT PULPING OF EUCALYPT

Range of Pulping Variables

Variables	Symbol	Range/level -1	Range/level 0	Range/level +1
Chemical charge (AA as Na_2O), %	X_1	15	16	17
Chip size, mm	X_6	(−12+6)		(−18+12)
Mean thickness, mm		2.5		3.5
Standard deviation		0.7		0.9

Constant Pulping Conditions

X_2 - Temperature, °C	165
X_3 - Sulfidity, %	21
X_4 - Liquor-to-wood ratio	3.6
X_5 - Time, min	60
X_7 - Time-to-temperature, min	90

TABLE 5.6: INFLUENCE OF CHEMICAL CHARGE AND CHIP SIZE ON THE KRAFT PULPING OF EUCALYPT

A. Pulping Conditions and Results

Expt. No.	Pulping conditions		Pulping results	
	Chemical charge,%	Chip thickness, mm	Yield,%	Kappa no.
E-11	15	2.5	49.6	34.8
E-12	16	2.5	48.1	36.8
E-13	17	2.5	48.4	28.2
E-14	15	3.5	51.5	33.6
E-15	16	3.5	48.5	39.1
E-16	17	3.5	48.7	31.9

B. Estimates of Effects by Yates's Algorithm

Effect	Yield	Kappa no.
Chemical charge:		
Linear	-1.00	-2.07
Quadratic	+1.25	-5.80
Chip thickness	+0.87	+1.60

chemical charge has a pronounced decreasing effect on yield whereas the effect on Kappa number is more towards higher levels of chemical charge.

Experiments were also conducted with mill run chips (thickness range 1.5-5.6 mm) (E-61, E-62) using conditions similar to runs E-12 and E-15, Table 5.7. Mill run chips gave yield and Kappa number comparable to the fractionated chips showing that pulp quality remains essentially the same in both the cases. These observations show that chip thickness (2-6 mm) is not a significant variable during kraft pulping of the eucalypt chips used in this investigation.

The chip fraction (-25 + 16 mm) with average chip thickness of 4.4 mm was selected for the 32 runs of the main experimental design in subsequent study dealing with the effect of five major pulping variables.

5.1.3 Fractional Factorial Design:

The influence of the remaining five major pulping variables (chemical charge, temperature, sulfidity, liquor-to-wood ratio, and pulping time) can be studied by using a sequential experimental design. A complete factorial design would require 32 runs, at two levels of each variable. Yates's algorithm can be adopted to estimate the 32 statistics consisting of one average value, 5 main effects, 10 two-factor interactions, 10 three-factor interactions, 5 four-factor interactions, and one five-factor interaction. Quite often it is observed that

TABLE 5.7: KRAFT PULPING OF EUCALYPT MILL RUN CHIPS

Pulping conditions:

X_1 - Chemical charge, (AA), % Na_2O	16
X_2 - Temperature, °C	165
X_3 - Sulfidity, %	21
X_4 - Liquor-to-wood ratio	3.6
X_5 - Time-at-temperature, min	60
X_7 - Time-to-temperature, min	90
X_6 - Chip thickness, mm	1.5-5.6

Pulping Results	E-61	E-62	Average	Average CPC*
Pulp yield, %	49.54	49.22	49.38	49.7
Black liquor solids,%	22.14	20.34	21.24	21.7
AA consumption, %	15.10	13.43	14.26	13.9
Kappa no.	41.39	37.10	39.24	31.7
Burst index, (kPa.m^2/g)	5.20	3.81	4.51	5.19
Tear index, (mN. m^2/g)	8.09	7.90	8.00	8.27
Tensile index,(N. m/g)	71.03	59.84	65.44	70.44
Folding endurance	357	44	201	304

*Average of the six experiments replicated at the central point conditions in the main design (E-47 to E-52), chip thickness: 4.4 mm

the absolute magnitude of the various effects decreases in the order (disregarding the effects of experimental error) - main effects, two factor interactions, three-factor interactions, and so on. Thus, at some point, higher order interactions which tend to become negligible can be deleted. Application of Yates's algorithm would require a redundancy of half of the statistics of a full factorial design. It is then possible to adopt fractional factorial designs to estimate the remaining effects and interactions. In this study a half-fraction factorial design (2^{5-1}) of the full 2^5 factorial requiring only 16 experiments is used.

The first five columns of Table 5.8 give the experimental design for a 2^{5-1} fractional factorial. The column of signs of variable 5 (time) has been obtained by multiplying the signs of columns 1 to 4. The remaining ten columns in Table 5.8 refer to the signs for calculating the two-factor interaction terms. The signs of the other interaction terms can be obtained in a similar manner. It can then be shown that the two-factor interactions are confounded by the three-factor interactions and the four-factor interactions are confounded by the main effects. The confounding pattern for all the three-factor and four-factor interactions with their aliases are shown in Table 5.9. The five-factor interaction (12345 = I) gives all positive signs and is used to find the average of all the runs. (Box et al., 1978).

TABLE 5.8: MULTIPLIERS FOR THE CALCULATION OF MAIN EFFECTS AND INTERACTIONS FOR A 2^{5-1} FRACTIONAL FACTORIAL DESIGN

(Table of Contrast Coefficients)

Run No.	Design matrix (main effects)					Interactions									
	1	2	3	4	5	12	13	14	15	23	24	25	34	35	45
1	-	-	-	-	+	+	+	+	-	+	+	-	+	-	-
2	+	-	-	-	-	-	-	-	-	+	+	+	+	+	+
3	-	+	-	-	-	-	+	+	+	-	-	-	+	+	+
4	+	+	-	-	+	+	-	-	+	-	-	+	+	-	-
5	-	-	+	-	-	+	-	+	+	-	+	+	-	-	+
6	+	-	+	-	+	-	+	-	+	-	+	-	-	+	-
7	-	+	+	-	+	-	-	+	-	+	-	+	-	+	-
8	+	+	+	-	-	+	+	-	-	+	-	-	-	-	+
9	-	-	-	+	-	+	+	-	+	+	-	+	-	+	-
10	+	-	-	+	+	-	-	+	+	+	-	-	-	-	+
11	-	+	-	+	+	-	+	-	-	-	+	+	-	-	+
12	+	+	-	+	-	+	-	+	-	-	+	-	-	+	-
13	-	-	+	+	+	+	-	-	-	-	-	-	+	+	+
14	+	-	+	+	-	-	+	+	-	-	-	+	+	-	-
15	-	+	+	+	-	-	-	-	+	+	+	-	+	-	-
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

The numerals (1,2,3,4,5) refer to the five variables

TABLE 5.9: CONFOUNDING PATTERN AND ESTIMATES FOR 2^{5-1} FRACTIONAL FACTORIAL DESIGN

Ralationship between column pairs*
1 = 2345
2 = 1345
3 = 1245
4 = 1235
5 = 1234
12 = 345
13 = 245
14 = 235
15 = 234
23 = 145
24 = 135
25 = 134
34 = 125
35 = 124
45 = 123
(I = 12345)

*The numerals (1,2,3,4,5) refer to the five variables

Thus the 16 statistics can be calculated from the 16 experiments of the fractional factorial design. A computer progra was developed (Appendix VII) for analysing all the data by Yates's algorithm for any 2^k complete factorial design.

Table 5.10 gives the coded levels and the actual values of the five variables for the half-fraction factorial design (E-21 to E-36). The coded forms of the input variable have been obtained from the following equation (5.1):

$$
\begin{aligned}
x_1 &= (\text{active alkali charge} - 16.0)/1.0 \\
x_2 &= (\text{Temperature} - 165.0)/5.0 \\
x_3 &= (\text{Sulfidity} - 21.0)/3.0 \\
x_4 &= (\text{Liquor:wood} - 3.6)/0.3 \\
x_5 &= (\text{Time} - 60.0)/15.0
\end{aligned}
\qquad (5.1)
$$

The heating period was maintained constant at 90 min. and fractionated chips were used (-25 + 16 mm) for the experimen Pulping conditions and results are given in Table 5.11. A typical computer output of Yates's analysis for pulp yield is given in Table 5.12, which gives the estimates of the ma and interaction effects of the variables. Table 5.13 gives the confounding pattern of the factorial design with four-factors and the corresponding half-fractional factorial design with 5 factors. The calculated estimates now show the main and two-factor interaction effects of the five pulping variables. An estimate of the experimental error is necessary to determine the statistical significance of th observed effects.

TABLE 5.10: PULPING VARIABLES AT DESIGN LEVELS AND CONSTANTS

Fractional-Factorial Design

Variables	Symbol	Range/levels* -1	+1
Chemical charge, (AA as % Na_2O)	X_1	15	17
Temperature, °C	X_2	160	170
Sulfidity, %	X_3	18	24
Liquor:wood	X_4	3.3	3.9
Time, min	X_5	45	75

*Coded levels (equation 3.1)

Constants: Chip fraction, mm -25+16

(Average chip thickness - 4.4 mm)

Time-to-temperature, min 90

TABLE 5.11: PULPING CONDITIONS AND EXPERIMENTAL RESULTS FOR THE KRAFT PULPING OF EUCALYPT: FRACTIONAL FACTORIAL DESIGN

Expt. No.	Pulping conditions					Experimental results	
	Chemical charge,%	Temperature °C	Sulfidity %	Liquor:wood	Time, min	Pulp yield %	Kappa no.
E-21	15	160	18	3.3	75	50.00	36.47
E-22	17	160	18	3.3	45	49.80	29.30
E-23	15	170	18	3.3	45	48.70	30.10
E-24	17	170	18	3.3	75	47.20	23.20
E-25	15	160	24	3.3	45	54.20	46.30
E-26	17	160	24	3.3	75	47.56	34.80
E-27	15	170	24	3.3	75	47.17	29.33
E-28	17	170	24	3.3	45	47.30	26.25
E-29	15	160	18	3.9	45	51.15	33.68
E-30	17	160	18	3.9	75	48.15	26.25
E-31	15	170	18	3.9	75	48.57	28.36
E-32	17	170	18	3.9	45	48.00	30.89
E-33	15	160	24	3.9	75	48.80	31.44
E-34	17	160	24	3.9	45	48.75	35.93
E-35	15	170	24	3.9	45	52.04	31.67
E-36	17	170	24	3.9	75	46.00	23.95

TABLE 5.12: KRAFT PULPING OF EUCALYPT: FRACTIONAL FACTORIAL DESIGN

YATES'S ALGORITHM FOR TOTAL PULP YIELD

Expt. No.	Response (y)	Algorithm (1)	(2)	(3)	(4)	Divisor	Estimate	Identi- cation
1	50.00	99.80	195.70	391.93	783.39	16	48.96	Average
2	49.80	95.90	196.23	391.46	-17.87	8	-2.23	1
3	48.70	101.76	195.87	-8.21	-13.43	8	-1.68	2
4	47.20	94.47	195.59	-9.66	1.91	8	0.24	12
5	54.20	99.30	-1.70	-11.19	0.25	8	0.03	3
6	47.56	96.57	-6.51	- 2.24	- 7.33	8	-0.92	13
7	47.17	97.55	-3.57	5.47	-0.17	8	-0.02	23
8	47.20	98.04	-6.09	-3.56	-0.35	8	-0.04	45
9	51.15	-0.20	-3.10	0.53	-0.47	8	-0.06	4
10	48.15	-1.50	-7.29	-0.28	-1.45	8	-0.18	14
11	48.57	-6.64	-2.73	-4.81	8.95	8	1.12	24
12	48.00	0.13	0.49	-2.52	-9.03	8	-1.13	35
13	48.80	-3.00	-1.30	-3.39	-0.81	8	-0.10	34
14	48.75	-0.57	6.77	3.22	2.29	8	0.29	25
15	52.04	-0.05	2.43	8.07	6.61	8	0.83	15
16	46.00	-6.04	-5.99	-8.42	-16.49	8	-2.06	5

TABLE 5.13: MAIN AND INTERACTION EFFECTS OF VARIABLES ON PULP YIELD

Expt. No.	Design run no.	Estimate	Identification: Complete factorial (4-factor)	Identification: Fractional factorial (5-factor) (5=1234)	Remarks
E-21	1	48.96	Average	Average	Yield
E-22	2	-2.23	1	1[c]	AA
E-23	3	-1.68	2	2[c]	T
E-24	4	0.24	12	12	AA x T
E-25	5	0.03	3	3	S
E-26	6	-0.92	13	13	AA x S
E-27	7	-0.02	23	23	T x S
E-28	8	-0.04	123[a,b]	45	D x t
E-29	9	-0.06	4	4	D
E-30	10	-0.18	14	14	AA x D
E-31	11	1.12	24	24[c]	T x D
E-32	12	-1.13	124[a,b]	35[c]	S x t
E-33	13	-1.10	34	34[c]	S x D
E-34	14	0.29	134[a,b]	25	T x t
E-35	15	0.83	234[a,b]	15	AA x t
E-36	16	-2.06	1234[a,b]	5[c]	t

a - Three-factor and four-factor interactions used for an indirect estimate of the experimental error (σ= 1.122)

b - replaced by aliases for the 5-factor design

c - statistically significant effect

Since no experiment in the above design was replicated, an indirect estimate of the error variance can be obtained if all the three-factor and four-factor interactions are assumed to be negligible and the observed higher-order interactions used to measure the differences arising mainly from experimental error (Box et al., 1978). An estimate of the error variance of pulp yield (1.259) is obtained as the quotient of the sum of squares of the effects and degrees of freedom. A comparison of the estimated standard error (1.122) and the observed effects in Table 5.13 shows the significance of three main and three interaction effects marked with 'C' as superscript. Table 5.14 gives similar results of Yates's analysis of Kappa number for these experiments, with an estimated standard error of 1.97. Table 5.15 gives the confounding pattern of factorial design with 4-factors and the corresponding half-fractional factorial design with 5 factors. Significant main and interaction effects are marked with 'C' as superscript. The above estimates of standard errors are in good agreement with the results from six replicate determinations (E-47 to E-52), conducted subsequently; yield - 0.68 vs 1.122 and Kappa number -1.85 vs 1.972.

Analysis of the results leads to the following observations on the effect of the pulping variables on yield and Kappa number.

TABLE 5.14: KRAFT PULPING OF EUCALYPT: FRACTIONAL FACTORIAL DESIGN

YATES'S ALGORITHM FOR KAPPA NUMBER

Expt. No.	Response (y)	Algorithm (1)	(2)	(3)	(4)	Divisor	Estimate	Identification
1	36.47	65.77	119.07	255.75	497.92	16	31.12	Average
2	29.30	53.30	136.68	242.17	-36.78	8	-4.60	1
3	30.10	81.10	119.18	-28.65	-50.42	8	-6.30	2
4	23.20	55.58	122.99	- 8.13	6.44	8	0.81	12
5	46.30	59.93	-14.07	-37.99	21.42	8	2.68	3
6	34.80	59.25	-14.58	-12.43	1.16	8	0.14	13
7	29.33	67.37	-4.90	8.69	-24.12	8	-3.02	23
8	26.25	55.62	-3.23	-2.25	-14.02	8	-1.75	45
9	33.68	-7.17	-12.47	17.61	-13.58	8	-1.70	4
10	26.25	-6.90	-25.52	3.81	20.52	8	2.57	14
11	28.36	-11.50	-0.68	-0.51	25.56	8	3.20	24
12	30.89	-3.08	-11.75	1.67	-10.94	8	-1.37	35
13	31.44	-7.42	0.27	-13.05	-13.80	8	-1.73	34
14	35.93	2.53	8.42	-11.07	2.18	8	0.27	25
15	31.67	4.49	9.96	8.15	1.98	8	0.25	15
16	23.95	-7.72	-12.21	-22.17	-30.32	8	-3.79	5

TABLE 5.15: MAIN AND INTERACTION EFFECTS OF VARIABLES ON KAPPA NUMBER

Expt. No.	Design run no.	Estimate	Identification		
			Complete factorial (4-factor)	Fractional factorial (5-factor) (5=1234)	Remarks
E-21	1	31.12	Average	Average	Kappa no.
E-22	2	-4.60	1	1[c]	AA
E-23	3	-6.30	2	2[c]	T
E-24	4	0.81	12	12	AA x T
E-25	5	2.68	3	3[c]	S
E-26	6	0.14	13	13	AA x S
E-27	7	-3.02	23	23[c]	T x S
E-28	8	-1.75	123[a,b]	45	D x t
E-29	9	-1.70	4	4	D
E-30	10	2.56	14	14[c]	AA x D
E-31	11	3.20	24	24[c]	T x D
E-32	12	-1.37	124[a,b]	35	S x t
E-33	13	-1.73	34	34	S x D
E-34	14	0.27	134[a,b]	25	T x t
E-35	15	0.25	234[a,b]	15	AA x t
E-36	16	-3.79	1234[a,b]	5[c]	t

a - Three-factor and four-factor interactions used for an indirect estimate of the experimental error (σ = 1.972)

b - replaced by aliases for the 5-factor design

c - statistically significant effect

Pulp Yield: Chemical charge, temperature and time are observed to have a significant effect on pulp yield. An increase in chemical charge (15 to 17 per cent) decreases pulp yield by 2.2 per cent and pulping time (45-75 min.) decreases pulp yield by 2 per cent, whereas an increase in cooking temperature from 160 to 170°C decreases yield by 1.7 per cent. The effects of sulfidity and liquor-to-wood ratio are negligible in the range studied. Although the interaction terms are not statistically significant, sulfidity x time, temperature x liquor-to-wood ratio, and chemical charge x sulfidity appear to have an appreciable effect on yield.

Kappa Number: Temperature, chemical charge, time and sulfidity are observed to have a strong effect on Kappa number. An increase in temperature (160-170°C) decreases Kappa number by 6.3 points, chemical charge (15-17 per cent) by 4.6 points and time (45-75 min.) by 3.8 points; an increase in sulfidity (18-24 per cent) increases Kappa number by 2.7 points. At constant active alkali, an increase in sulfidity results in a decrease in effective alkali - the active pulping chemical. This results in a slight increase in pulp yield and is accompanied by an increase in Kappa number (Kleppe, 1970; Bailey et al., 1969). The interaction effect between temperature and sulfidity is also important. Liquor-to-wood ratio although having no direct influence on Kappa number, appears to have an interaction effect with chemical charge and temperature.

5.1.4 Second-Order Central Composite Rotatable Design:

Analysis of the data by Yates's method has shown that pulp yield is significantly influenced by chemical charge, temperature and time, and that Kappa number is strongly affected by chemical charge, temperature, time and sulfidity; analysis also showed moderate interaction effects among the five variables over the range studied. However, over a wider range of the variables, the influence of sulfidity and liquor-to-wood ratio, and some of the interaction effects could also become predominant. Response surface methods would be appropriate for such studies. The fractional factorial design for five factors can be suitably augumented by adding further experiments; six experiments at the central point conditions and ten runs at the star points would form a second-order central composite rotatable design (section 3.2). The response surface obtained from such designs can be used for a thorough exploration of the experimental range. It can also be used to obtain contour plots and for the optimization of the pulping parameters.

5.1.4.1 Regression Analysis of Experimental Data: The full experimental range of the second-order central point composite design is given in Table 5.16. Pulping conditions and the experimental results are given in Table 5.17 and 5.18, respectively. The average value and the standard deviation in the observed data for the six replicate experiments

TABLE 5.16: KRAFT PULPING OF EUCALYPTS
PULPING VARIABLES AT DESIGN LEVELS AND CONSTANTS
SECOND ORDER CENTRAL COMPOSITE ROTATABLE DESIGN

Variables	Symbol	Range/Levels[a]				
		-2	-1	0	+1	+2
Chemical charge (AA) as Na_2O, %	X_1	14	15	16	17	18
Temperature, °C	X_2	155	160	165	170	175
Sulfidity, %	X_3	15	18	21	24	27
Liquor:wood	X_4	3.0	3.3	3.6	3.9	4.2
Time, min.	X_5	30	45	60	75	90

[a]Levels refer to Box's statistical design

Constants: Chip fraction, mm -25 +16
(Average chip thickness - 4.4 mm)
Time-to-temperature, min 90

TABLE 5.17: KRAFT PULPING OF EUCALYPT

PULPING CONDITIONS

Expt. no. (1)	Chemical charge,% X_1 (2)	Tempera-ture, °C X_2 (3)	Sulfidity, % X_2 (4)	Liquor-to-wood ratio X_4 (5)	Pulping time, mi X_5 (6)
E-21	15	160	18	3.3	75
E-22	17	160	18	3.3	45
E-23	15	170	18	3.3	45
E-24	17	170	18	3.3	75
E-25	15	160	24	3.3	45
E-26	17	160	24	3.3	75
E-27	15	170	24	3.3	75
E-28	17	170	24	3.3	45
E-29	15	160	18	3.9	45
E-30	17	160	18	3.9	75
E-31	15	170	18	3.9	75
E-32	17	170	18	3.9	45
E-33	15	160	24	3.9	75
E-34	17	160	24	3.9	45
E-35	15	170	24	3.9	45
E-36	17	170	24	3.9	75
E-37	14	165	21	3.6	60
E-38	18	165	21	3.6	60
E-39	16	155	21	3.6	60

Table 5.17 contd.

(1)	(2)	(3)	(4)	(5)	(6)
E-40	16	175	21	3.6	60
E-41	16	165	15	3.6	60
E-42	16	165	27	3.6	60
E-43	16	165	21	3.0	60
E-44	16	165	21	4.2	60
E-45	16	165	21	3.6	30
E-46	16	165	21	3.6	90
E-47	16	165	21	3.6	60
E-48	16	165	21	3.6	60
E-49	16	165	21	3.6	60
E-50	16	165	21	3.6	60
E-51	16	165	21	3.6	60
E-52	16	165	21	3.6	60

TABLE 5.18: KRAFT PULPING OF EUCALYPT

PULPING RESULTS

Expt. no.	Experimental Results			Strength Properties		
	Pulp yield, %	Black liquor solids, %	Kappa no.	Burst index, $kPa.m^2/g$	Tear index, $mN. m^2/g$	Tensile index, N. m/g
(1)	(2)	(3)	(4)	(5)	(6)	(7)
E-21	50.00	24.17	36.47	4.96	7.41	72.08
E-22	49.80	24.43	29.30	5.45	6.90	77.09
E-23	48.70	22.84	30.10	6.20	8.01	80.22
E-24	47.20	27.39	23.20	5.39	6.97	55.90
E-25	54.20	23.13	46.30	4.80	7.59	73.65
E-26	47.56	23.15	34.80	5.34	6.75	83.55
E-27	47.17	23.53	29.33	6.25	6.75	90.91
E-28	47.30	25.07	26.25	5.59	6.42	89.05
E-29	51.15	19.63	33.68	5.40	8.30	80.12
E-30	48.15	19.40	26.25	5.76	5.60	87.28
E-31	48.57	19.95	28.36	5.87	7.31	66.23
E-32	48.00	20.11	30.89	6.00	8.41	76.59
E-33	48.80	19.47	31.44	5.73	8.86	85.32
E-34	48.75	20.25	35.93	5.50	8.65	75.02
E-35	52.04	21.00	31.67	6.74	7.83	87.38
E-36	46.00	20.58	23.95	5.59	8.24	75.42
E-37	50.75	20.70	31.44	6.65	7.23	76.69
E-38	45.80	24.50	27.02	5.85	7.80	78.26

Table 5.18 contd

(1)	(2)	(3)	(4)	(5)	(6)	(7)
E-39	51.80	20.82	33.24	5.28	8.05	68.58
E-40	46.59	23.05	25.62	5.41	6.88	85.64
E-41	49.22	21.81	30.89	4.26	9.00	64.33
E-42	48.81	19.95	32.56	5.71	7.72	85.42
E-43	47.35	22.84	26.25	5.73	8.57	76.59
E-44	49.25	19.00	31.44	5.91	7.29	83.75
E-45	50.30	21.40	51.11	5.34	7.35	68.45
E-46	47.36	23.45	29.33	6.70	4.96	88.36
E-47	50.41	21.76	30.70	6.16	8.86	71.70
E-48	49.92	22.26	29.66	5.45	8.54	67.17
E-49	50.25	21.96	30.57	4.82	8.17	66.03
E-50	49.69	20.42	31.14	5.24	8.31	79.45
E-51	48.51	22.26	33.58	4.46	8.04	71.38
E-52	49.44	21.68	34.30	5.02	7.71	66.93

(E-47 to E-52) conducted at the central point conditions are given in Table 5.19. The range of the dependent variables observed is also given in Table 5.19 and a comparison with the estimated error shows that all the responses are statistically significant.

Linear regression equations gave a poor fit and a second order model (equation A.8) of the experimental data was subsequently fitted. Pulp yield (Y) is represented by equation (5.2).

$$\begin{aligned} Y = {} & 49.62 - 1.157x_1 - 0.994x_2 - 0.024x_3 + 0.139x_4 \\ & -0.932x_5 - 0.269x_1^2 - 0.039x_2^2 - 0.084x_3^2 - 0.263x_4^2 \\ & -0.130x_5^2 + 0.119x_1x_2 - 0.458x_1x_3 - 0.091x_1x_4 \\ & +0.413x_1x_5 - 0.011x_2x_3 + 0.559x_2x_4 + 0.143x_2x_5 \\ & -0.051x_3x_4 - 0.564x_3x_5 - 0.022x_4x_5 \qquad (5.2) \\ & (R^2 = 0.94;\ F = 8.3 \quad d.f. = 11) \end{aligned}$$

Similar regression equations were obtained for Kappa number, black liquor solids and the strength properties - burst index, tear index and tensile index. The twentyone coefficients were estimated by the method of least squares (Appendix I, VIII) and the results are summarized in Table 5.20. The general second-order model (equation 5.3) is reproduced in Table 5.18. The regression equations showed good reliability of the second order models for pulp yield, Kappa number and black liquor solids with R^2 = 0.94, 0.86 and 0.89 respectively. Accountability for the strength

TABLE 5.19: MEAN AND STANDARD DEVIATION OF THE OBSERVED DATA FOR THE SIX REPLICATED EXPERIMENTS AT THE CENTRAL POINT CONDITIONS AND THE OVERALL RANGE OF THE DEPENDENT VARIABLES

Dependent Variable	Mean and standard deviation		Overall range of dependent variables	
	Mean	Std.deviation	Range	Total variation
Pulp yield, %	49.70	0.68	45.8 - 54.2	8.4
Black liquor solids, %	21.73	0.68	19.0 - 24.43	5.43
Active alkali consumption,%	13.85	0.47	-	-
Kappa number	31.66	1.85	23.2 - 51.1	28.9
Burst index, (kPa m^2/g)	5.19	0.59	4.26 - 6.74	2.48
Tear index, (mN. m^2/g)	8.27	0.40	5.6 - 9.0	3.40
Tensile index,(N. m/g)	70.44	5.02	55.9 - 90.9	35.00

TABLE 5.20: KRAFT PULPING OF EUCALYPT MATHEMATICAL MODELS

Parameter	Coefficients					
	Pulp yield	Black liquor solids	Kappa no.	Burst index	Tear index	Tensile index
(1)	(2)	(3)	(4)	(5)	(6)	(7)
b_o	49.615	21.652	31.809	5.218	8.233	70.609
b_1	-1.157	0.594	-1.901	-0.122	-0.124	-0.536
b_2	-0.994	0.471	-2.736	0.206	-0.103	0.905
b_3	-0.024	-0.228	1.032	0.142	-0.016	4.457
b_4	0.139	-1.708	-0.133	0.124	0.160	1.051
b_5	-0.932	0.233	-3.078	0.080	-0.375	0.725
b_6	-0.269	0.291	-0.758	0.238	-0.151	1.593
b_{22}	-0.039	0.124	-0.708	0.012	-0.163	1.501
b_{33}	-0.084	-0.140	-0.134	-0.078	0.061	0.943
b_{44}	-0.263	-0.130	-0.854	0.131	-0.047	2.266
b_{55}	-0.130	0.227	1.990	0.181	-0.491	1.825
b_{12}	0.119	0.313	0.403	-0.228	0.275	-2.472
b_{13}	-0.458	-0.176	0.073	-0.109	0.136	-0.777
b_{14}	-0.091	-0.380	1.283	-0.028	0.083	0.408
b_{15}	0.413	0.009	0.124	-0.008	-0.089	-0.548
b_{23}	-0.011	0.095	-1.508	0.057	-0.319	3.928
b_{24}	0.559	-0.066	1.598	-0.067	0.055	-1.989
b_{25}	0.143	0.230	0.136	-0.129	0.089	-4.196
b_{34}	-0.051	0.385	-0.863	0.034	0.359	-2.434

Table 5.20 contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
b_{35}	-0.564	-0.414	-0.684	0.084	0.278	2.664
b_{45}	-0.022	-0.273	-0.876	-0.037	-0.134	0.794
R^2	0.9381	0.8870	0.8644	0.6567	0.7473	0.7796
F-ratio	8.3355	4.3155	3.5055	1.0521	1.6261	1.9398

$$y = b_o + \sum_{1}^{k} b_i x_i + \sum_{1}^{k} b_{ii} x_i^2 + \sum_{i \ j}^{k} b_{ij} \, x_i \, x_j \tag{5.3}$$

properties was only **fair** with $R^2 = 0.66$, 0.75 and 0.80 for burst index, tear index and tensile index respectively. Bailey et al. (1969) and McKibbins (1970) also have reported similar correlation coefficients of pulp strength properties with the pulping process variables. The low correlation coefficient for strength properties indicates the possible influence of additional parameters besides the five digester variables considered. The factors which would influence pulp strength properties are the possible inevitable variations associated with the post-treatment of the pulp from the digestion step, such as beater operation, hand sheet preparation and conditioning, and sensitivity and precision of the testing equipment used.

Hatton et al. (1972) have observed that the precision of yield determinations is much greater than the routine pulp strength tests. In this study, equipment in a mill control laboratory were used for all the post treatment steps and to determine the strength properties. The variables associated with pulp post treatments for strength determinations would require a detailed study of each step with test equipment of high precision. In this study, the five pulping variables considered account for three-fourths (66-80 per cent) of the total variation in strength properties and only one-quarter will be associated with post digestion treatments. Thus the second-order regression models can be considered to give an acceptable representation of the strength properties.

5.1.4.2 <u>Statistical Significance of Parameters:</u> The relative significance of the parameters in the models, equation (5.3) and Table 5.20 was evaluated using students''t' test. The results are summarized in Table 5.21 and the significant parameters (95 per cent confidence level for yield, Kappa number and black liquor solids and 90 per cent for the strength properties) are shown in parentheses for all the responses. Subsequently, only the statistically significant terms alone were retained to obtain a revised fit of the observed data as illustrated by equation (5.4) for pulp yield.

$$
\begin{aligned}
Y = {} & 49.398 - 1.157\,x_1 - 0.994x_2 - 0.932x_5 - 0.251x_1^2 \\
& -0.245x_4^2 - 0.458x_1x_3 + 0.413x_1x_5 + 0.559x_2x_4 \\
& -0.564x_3x_5 \qquad (5.4)
\end{aligned}
$$

$$(R^2 = 0.9201; \quad F = 28.147, \quad d.f. = 22)$$

A summary of the revised regression equations for the various observed responses is given in Table 5.22. The revised correlation coefficient was good for pulp yield (0.92 vs 0.94), satisfactory for Kappa number (0.84 vs 0.86) and black liquor solids (0.80 vs 0.89). The representation of the strength properties by the complete second-order model gave a better correlation coefficient. All the terms in the revised regression equations (Table 5.22) were confirmed to be statistically significant by the Students' 't' test. Thus the revised regression equations are recommended for reliable

TABLE 5.21: SIGNIFICANCE OF PARAMETERS

STUDENT'S t VALUES

Parameter	Computed 't' Values					
	pulp yield	Black liquor solids	Kappa no.	Burst index	Tear index	Tensile index
(1)	(2)	(3)	(4)	(5)	(6)	(7)
b_o	(64.750)[a]	(19.740)	(9.174)	(8.992)	(10.509)	(10.398)
b_1	(7.384)	(2.654)	(2.686)	(1.030)	0.777	0.337
b_2	(6.342)	(2.103)	(3.866)	(1.741)	0.641	0.652
b_3	0.151	1.016	(1.458)	(1.199)	0.010	(3.216)
b_4	0.886	(7.630)	0.188	(1.045)	(1.000)	0.758
b_5	(5.948)	1.042	(4.350)	0.678	(2.345)	0.523
b_{11}	(1.899)	(1.435)	(1.184)	(2.222)	(1.042)	(1.270)
b_{22}	0.276	0.613	1.105	0.109	(1.129)	(1.197)
b_{33}	0.594	0.688	0.209	0.731	0.419	0.752
b_{44}	(1.855)	0.639	(1.334)	(1.218)	0.324	(1.807)
b_{55}	0.920	1.120	(3.109)	(1.685)	(3.393)	(1.456)
b_{12}	0.622	1.139	0.464	(1.572)	(1.404)	(1.456)
b_{13}	(0.387)	0.643	0.084	0.719	0.696	0.457
b_{14}	0.472	(1.386)	(1.480)	0.194	0.421	0.240
b_{15}	(2.153)	0.032	0.143	0.056	0.453	0.323
b_{23}	0.055	0.346	(1.739)	0.392	(1.628)	(2.314)
b_{24}	(2.915)	0.241	(1.843)	0.461	0.280	(1.172)
b_{25}	0.746	0.838	0.157	0.892	0.453	(2.472)
b_{34}	0.264	(1.404)	0.995)	0.237	(1.832)	(1.434)

Table 5.21 contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
b_{35}	(2.941)	(1.509)	0.789	0.582	(1.417)	(1.569)
b_{45}	0.114	0.994	(1.011)	0.254	0.682	0.468

Tabulated 't' values

$$(t_{0.95,\ 11}) = 1.796$$

$$(t_{0.90,\ 11}) = 1.363$$

[a]Significant parameters in parenthesis

TABLE 5.22: KRAFT PULPING OF EUCALYPT

FINAL MATHEMATICAL MODEL WITH SIGNIFICANT PARAMETERS

Parameter (1)		Total pulp yield (2)	Black liquor solids (3)	Kappa no. (4)	Burst index (5)	Tear index (6)	Tensile index (7)
Intercept	b_o	49.400	21.718	31.675	5.157	8.246	71.551
x_1	b_1	-1.157	0.594	-1.901	-0.122		
x_2	b_2	-0.994	0.471	-2.736	0.206		
x_3	b_3			1.032	0.142		4.457
x_4	b_4		-1.708		0.124	0.160	
x_5	b_5	-0.932		-3.078		-0.375	
x_1^2	b_{11}	-0.251	0.285	-0.747	0.243	-0.152	1.514
x_2^2	b_{22}			-0.697		-0.164	1.423
x_3^2	b_{33}						
x_4^2	b_{44}	-0.245		-0.843	0.136		2.188
x_5^2	b_{55}			2.001	0.186	-0.492	1.747
x_1x_2	b_{12}				-0.228	0.275	-2.472
x_1x_3	b_{13}	-0.458					
x_1x_4	b_{14}		-0.380	1.283			
x_1x_5	b_{15}	0.413					
x_2x_3	b_{23}			-1.508		-0.319	3.928
x_2x_4	b_{24}	0.559		1.598			-1.989
x_2x_5	b_{25}						-4.196
x_3x_4	b_{34}		0.385			0.359	-2.434

Table 5.22 contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
x_3x_5 b_{35}	-0.564	-0.414			0.278	2.664
x_4x_5 b_{45}			-0.876			
R-squared	0.9201	0.8003	0.8402	0.5567	0.6795	0.7272
F-ratio	28.147	13.7417	8.3264	3.611	5.1837	4.8474
F-tabulated at 95%	2.94	3.41	2.56	3.13	2.94	2.65
d.f.	(22,9)	(24,7)	(19.12)	(23,8)	(22.9)	(20, 11)

estimates of yield and Kappa number, and the complete second order representation can give acceptable estimates of the pulp strength properties.

5.1.5 Miscellaneous Models:

In addition to the general second-order model (equation 5.3) developed in the previous section for the kraft pulping of eucalypt, various other models also were tried and the correlations were observed to be less satisfactory. The results of the various trials are summarized below.

1. A regression model fitted with effective alkali as used by Hatton (1972), Wallin and Noreus (1973), Hinrichs (1967) gave essentially the same correlation coefficients both for yield and Kappa number.
2. Regression model using the H-factor representing temperature and time interactions gave poor correlation coefficients for yield and Kappa number. Correlation of the data with Hatton's model [model 10, Table 2.2] and Chari's model [14, Table 2.2] also were not satisfactory.
3. The log models proposed by Chari (1973) and Lin et al. (1978), modified with the inclusion of sulfidity as a variable, also gave a poor fit of yield and Kappa number.

$$Y = 192.63 \frac{(D)^{0.0388}}{(AA)^{0.3722}\ (H)^{0.0555}\ (S)^{0.0054}}$$

$$(R^2 = 0.69)$$

$$K = 1277.5 \frac{(S)^{0.2036}\ (D)^{0.0321}}{(AA)^{0.9733}\ (H)^{0.2514}}$$

$$(R^2 = 0.543)$$

The low value of the exponent for sulfidity in the above expression shows a negligible effect on yield.

4. Hatton's model [10, Table 2.2] with effective alkali and H-factor as variables did not show any convergence.

The results of the above analysis show that the general second-order model [8, Table 2.2], equation 5.3 correlating the effects of the five pulping variables would give a satisfactory representation of the digester responses.

2.1.6 Effect of Pulping Variables on Pulp Properties:

Although it is quite difficult to recognize the influence of individual variables separately in such a complex system, the relative importance of each of them and their possible interactions with other variables can be judged from the magnitude of the coefficients. The effect of individual variables on pulp yield, Kappa number and strength properties is discussed below.

5.1.6.1 Pulp Yield: Equation (5.3) shows that chemical charge is the most important pulping variable influencing pulp yield. An increase in chemical charge reduces pulp yield; this may be partly attributed to the degradation of the higher xylan content of eucalypts. Temperature and time are observed to be the next important pulping variables. Hatton and Hejjas (1972) have also reported similar effects of chemical charge and temperature during the pulping of hardwoods. Sulfidity and liquor-to-wood ratio have shown no direct influence on pulp yield. Kleppe (1970) also has reported the negligible effect of sulfidity (15-40 per cent) on the yield of birch kraft pulp. The quadratic effect of liquor-to-wood ratio shows that very low or very high levels would tend to decrease pulp yield. Significant interactions are observed between liquor-to-wood ratio-temperature, chemical charge-sulfidity, and chemical charge-time. These results are very similar to the earlier observations based on Yates's analysis.

5.1.6.2 Kappa Number: Pulping time has the most significant influence on Kappa number as shown by the magnitude of the coefficients (b_5 and b_{55}) in the regression model. The other important pulping variables in the order of influence are temperature and chemical charge; an increase in either or both decreases Kappa number. Higher levels of chemical charge and temperature decrease Kappa number more than lower

levels. In the fractional factorial design where the range of the pulping variables was narrow, the order in which the pulping variables influenced Kappa number was - temperature, chemical charge and time. In the second-order central composite design with a wider range of variables, time becomes the most important variable. Increase in sulfidity at constant active alkali tends to increase the Kappa number and is in agreement with the results reported by Bailey et al. (1969) and Kleppe (1970). Liquor - to - wood ratio although not having a direct influence on Kappa number, interacts significantly with chemical charge, temperature and time. Interaction effect is also observed between temperature and sulfidity.

5.1.6.3 <u>Strength Properties</u>: Pulp strength properties are influenced by the progress of the pulping reactions which modify the internal properties of the constituent fibers. Thus, chemical charge, temperature, sulfidity and time which control the residual pulp lignin content would also influence the pulp strength properties. The role of sodium sulfide on yield and strength properties is illustrated by the results of soda and kraft pulping under similar conditions, Table 5.23. The Kappa number (54.3) and yield (57.07) of soda pulp are higher compared to Kappa number (31.7) and yield (49.47) of Kraft pulp. Burst, tear and tensile indices of soda pulps are lower compared to the eucalypt kraft pulp.

TABLE 5.23: PULPING OF EUCALYPT CHIPS BY SODA PROCESS

COMPARISON WITH KRAFT PULPS

Pulping conditions and Pulp properties	Soda pulping			Kraft pulping (E-47 to E-52)
	E-71	E-72	Average	
Pulping conditions				
Chemical charge (AA as Na_2O), %	16	16	16	16
Temperature, °C	165	165	165	165
Sulfidity, %	0	0	0	21
Liquor-to-wood ratio	3.6	3.6	3.6	3.6
Time, min	60	60	60	60
Chip size, range mm	16-25	16-25	16-25	16-25
Time-to-temperature, min.	90	90	90	90
Pulping Results				
Total pulp yield, %	56.88	57.2	57.04	49.70
Black liquor solids,%	20.23	20.03	20.13	21.72
AA consumption, %	-	-	-	13.85
Kappa no.	45.97	62.68	54.33	31.66
Strength properties				
Burst index, (kPa m^2/g)	3.23	3.02	3.13	5.19
Tear index, (mN m^2/g)	5.85	5.69	5.77	8.27
Tensile index, (N.m/g)	57.23	52.41	54.82	70.44
Folding endurance	39	19	29	304
Remarks			Very high rejects	Very small quantity of rejects

It would have been desirable to compare the pulps at the same Kappa number level; however, to obtain a Kappa number (31.7) comparable to the kraft digestion, soda pulping would require higher chemical charge, temperature and time with consequent polysaccharide degradation reactions.

A rigorous interpretation of the effects of the kraft pulping variables is difficult owing to the low correlation coefficients obtained for the regression equations of the strength properties; nevertheless, the following trends are observed from the parameters of the regression models.

1. Increase in chemical charge somewhat reduces the bursting and tensile strengths; tear index should have improved but it shows a slight decrease from the regression models.
2. Bursting and tensile strengths have improved with an increase in the other pulping variables studied.
3. Pulping time and sulfidity have shown maximum influence on tearing and tensile strengths respectively; the former reduces the tear index and the latter increases the tensile index according to the regression equations (5.3).
4. Linear effects of chemical charge, temperature and sulfidity on tear index are seen to be small; however the interaction terms suggest

that tear index increases with the progress of cooking - higher temperatures and sulfidity improving tear index.

The above trends are in agreement with the results reported by other workers on the effect of pulping variables on strength properties. The values of the strength properties obtained are comparable to the results reported by Phillips et al. (1967) and Higgins (1970) for Australian native eucalypts of comparable density (0.66 g cm^{-3}).

5.1.7 Optimum Pulping Conditions:

One of the principal uses of the regression models developed in the previous section was to locate the pulping conditions which would give an optimum yield of pulp with desired properties. Two computer programs for constrained optimization - "Complex Method of Box" and "Constrained Rosenbrock Method" were used and the latter was found to be efficient and reliable.

Several trial combinations of any two/three constraints from among yield, Kappa number and strength properties were used for the optimization study. The results of all the trials are summarized in Table 5.24. The objective was to maximize the response shown in column 2 (Table 5.24) subject to the constraints in column 3. The optimum pulping conditions and the estimates of the maximum value of the desired objective and other pulp properties obtainable are also given in Table 5.24.

TABLE 5.24: OPTIMIZATION OF KRAFT PULPING OF EUCALYPTS

Sl. No.	Objective function	Constraints and range	Optimum conditions: Chemical charge, %	Temp., °C	Sulfidity %	Liquor/ wood	Time, min.	Pulp properties at optimum
1.	Yield	BI = 4.4 - 5.4 Kappa = 29 - 35	14.2	155.0	24.5	3.70	42.1	Yield = 55.65 BI = 5.34 Kappa = 29.4
2.	Yield	BI = 4.4 - 5.4 TI = 7.3 - 8.4	14.7	166.0	15.0	4.15	60.0	Yield = 54.72 BI = 5.39 TI = 8.12
3.	Yield	BI = 4.4 - 5.4 TI = 7.8 - 8.4	15.6	159.0	21.5	3.64	48.0	Yield = 52.03 BI = 4.92 TI = 8.33
4.	BI	Yield = 48 - 50 TI = 7.8 - 8.4	14.1	166.0	27.0	3.79	69.3	Yield = 49.8 BI = 7.31 TI = 7.85
5.	BI	Yield = 48 - 50 Kappa = 27 - 33 TI = 7.8 - 8.5	15.8	170.0	23.3	3.70	59.2	Yield = 49.1 Kappa = 27.0 BI = 5.62 TI = 7.85
6.	TI	Yield = 43.0 - 47.5 Kappa = 27 - 33 BI = 4.4 - 6.4	16.8	170.0	20.7	3.63	56.7	Yield = 47.5 Kappa = 27.2 BI = 5.26 TI = 8.07

Kappa Kappa number of pulp
BI Burst index
TI Tear index

For example, in trial 3, the objective was to maximize pulp yield subject to the constraints on burst index and tear index in the range 4.4 - 5.4 and 7.8 - 8.4 respectively. The maximum yield was 52.0 per cent for the optimum conditions shown in the table; the burst index of the pulp was 4.92 and tear index was 8.33. In trial number 6, three constraints were introduced (yield: 43.0 - 47.5, Kappa number: 27-33, burst index: 4.4 - 6.4) and the pulping conditions determined for maximum tear index; the pulp had the following properties - yield = 47.5, Kappa number = 27.2, burst index = 5.26, and tear index = 8.07. These estimates (trial 6) of pulping conditions are close to the central point conditions of the main experimental design with slightly higher values of chemical charge and temperature.

Pulping experiments (E-81, E-82) were conducted in duplicate adopting the conditions of trial 6 and the results are summarized in Table 5.25. Table 5.25 also shows a comparison of the experimental results, estimates based on Constrained Rosenbrock Method, and the average values obtained for the experiments at central point conditions (E-47 to E-52). The results show very good agreement (98 per cent) for pulp yield and the agreement is within 10 per cent for Kappa number and pulp strength properties.

TABLE 5.25: KRAFT PULPING OF EUCALYPTS

OPTIMUM PULPING CONDITIONS AND PREDICTED RESPONSES

COMPARISON WITH THE ACTUAL PULPING RESULTS

Variables and Responses	Optimum Pulping Conditions				Central point conditions (E-47 to E-52)
	Estimates	E-81	E-82	Mean (Exptl)	
Constant conditions					
Chip size range, mm	-25+16	-25+16	-25+16	-	-25+16
Avg. thickness, mm	4.4	4.4	4.4	-	4.4
Time-to-temperature, min	90	90	90	-	90
Pulping variables					
Chemical charge, % Na_2O	16.8	16.8	16.8	-	16
Temperature, °C	170	170	170	-	165
Sulfidity, %	20.7	20.8	20.8	-	21
Liquor-to-wood ratio	3.63	3.6	3.6	-	3.6
Time, min	56.7	57	57	-	60
Responses					
Pulp yield, %	47.50	46.08	46.62	46.35	49.70
Black liquor solids, %	22.95	20.99	20.50	20.74	21.73
Kappa number	27.20	30.63	30.04	30.34	31.66
Burst index, kPa, m^2/g	5.26	5.62	6.11	5.87	6.19
Tear index, mN. m^2/g	8.07	7.18	7.17	7.18	8.27
Tensile index, N. m/g	75.61	80.47	81.37	80.92	70.44
	DF	488	595	541	304

5.1.8 Representation of the Response Surface:

The regression models, equation (5.3), can be represented geometrically as a response surface. The interpretation of the results as a response surface, with only two x-variables is facilitated by plotting the contours of equal response. To draw a given contour, y is set equal to a given response level and the equation is solved as a quadratic in x_2 for selected values of x_1 to obtain a series of points (x_1, x_2) on the contour.

With three x-variables, a three-dimensional representation is necessary with one variable selected along the vertical (x_3) and the contours (x_1,x_2) can be located at different heights. If there are more than three x-variables, geometrical representation can be used only partially. In such cases the response surface can be transformed to its canonical form. Canonical analysis involves a shifting of the origin to a new location (optimum) and rotation of the axes to correspond to the contour axes. It is useful in the analysis and geometrical representation of multivariable systems involving complicated maxima/minima.

5.1.8.1 Univariate Representations: Univariate representation of response surface (Hinrichs, 1967; Mathur and Peterson, 1978) has an important practical utility. It can be used to estimate the changes in the observed response caused by one of the input variables, while the digester is operating under a

set of desired (optimum) conditions. This can also be used in evolutionary operations to improve digester operation to obtain the desired pulp properties. Figures 5.1 - 5.6 were obtained by the regression equation models (Table 5.20) for the responses while keeping all variables at the optimum conditions and varying only one at a time in the full range of the experimental region.

Figure 5.1 shows the effect of change in cooking conditions on pulp yield. Active alkali (chemical charge) has the maximum influence on yield with a steeper slope at higher alkali charge levels. Yield shows essentially linear dependence on temperature and sulfidity. At the optimum conditions, change in cooking time seems to have virtually no effect on the pulp yield. Increasing liquor-to-wood ratio increases pulp yield because of dilution of pulping chemicals. The effect of all pulping variables on pulp yield is in agreement with the previous studies on the general behaviour of hardwoods.

The influence on black liquor solids is shown in Figure 5.2 and the observed effects complement the behaviour obtained for pulp yield confirming the consistency of latter data.

Figure 5.3 shows the effect of pulping variables on Kappa number and pulping time has the dominant influence. Kappa number shows a minimum at 65-70 min compared to the

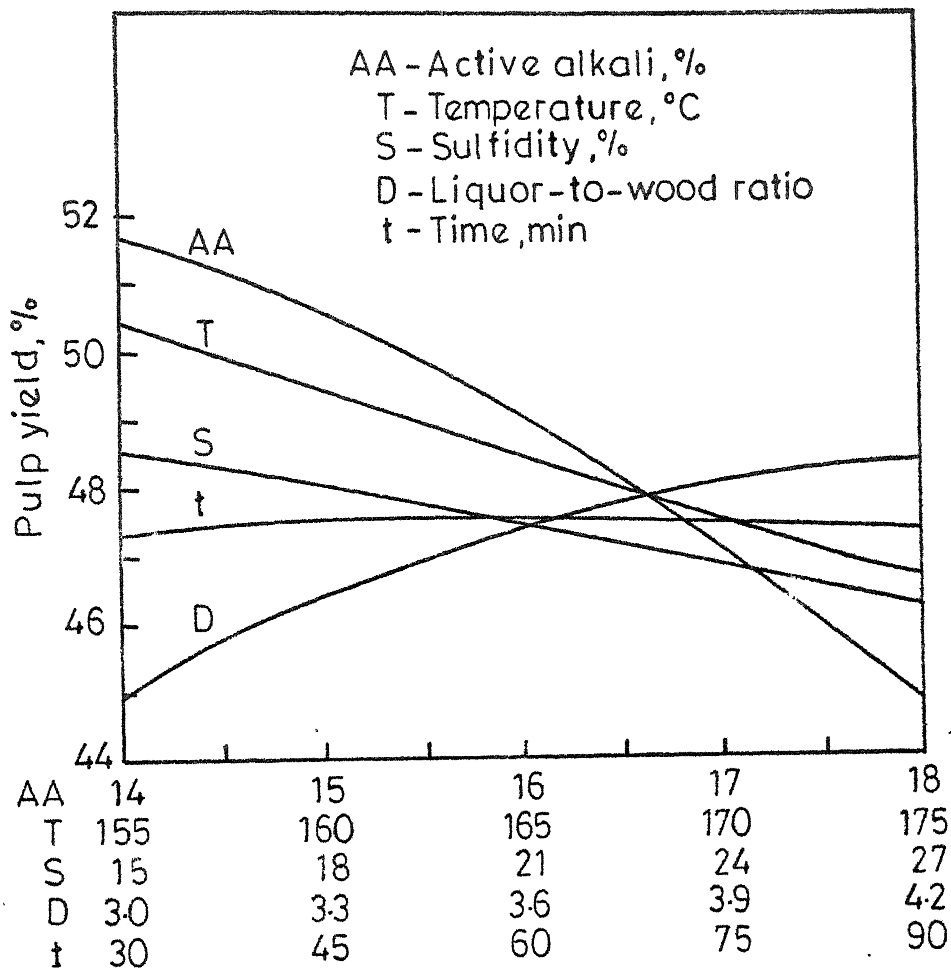


Fig 5.1 - Univariate representation of response surface for eucalypt pulp yield.

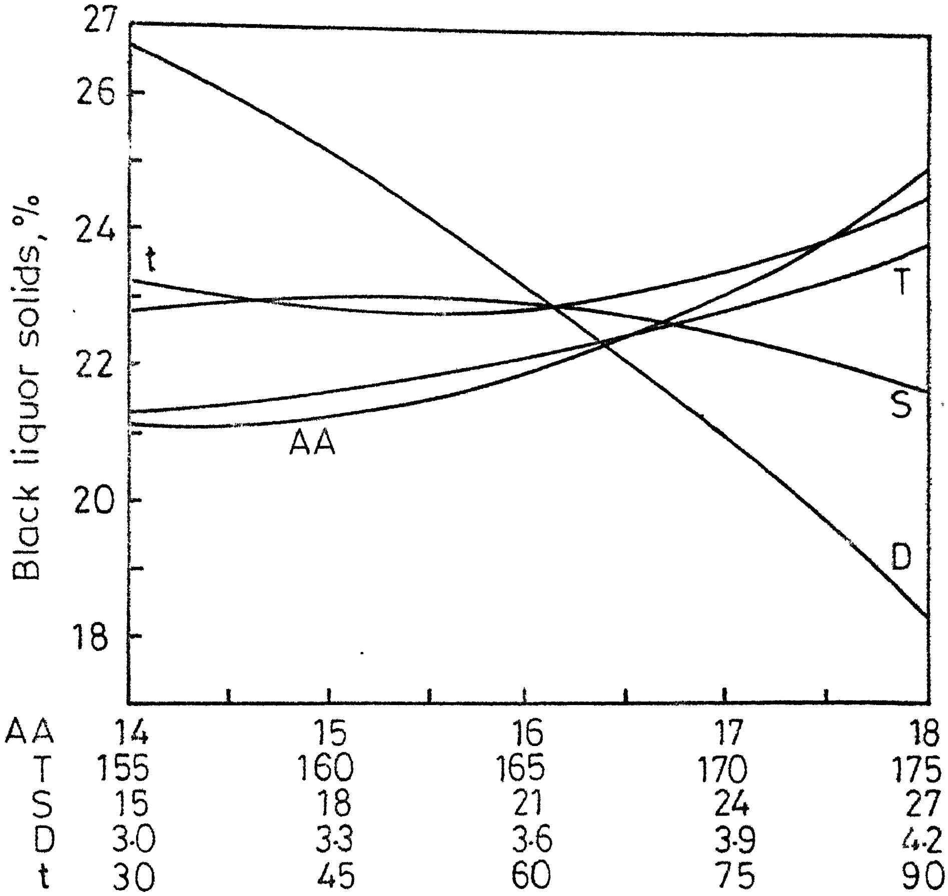


Fig. 5·2 - Univariate representation o: response surface for black·liquor solids (eucalypt).

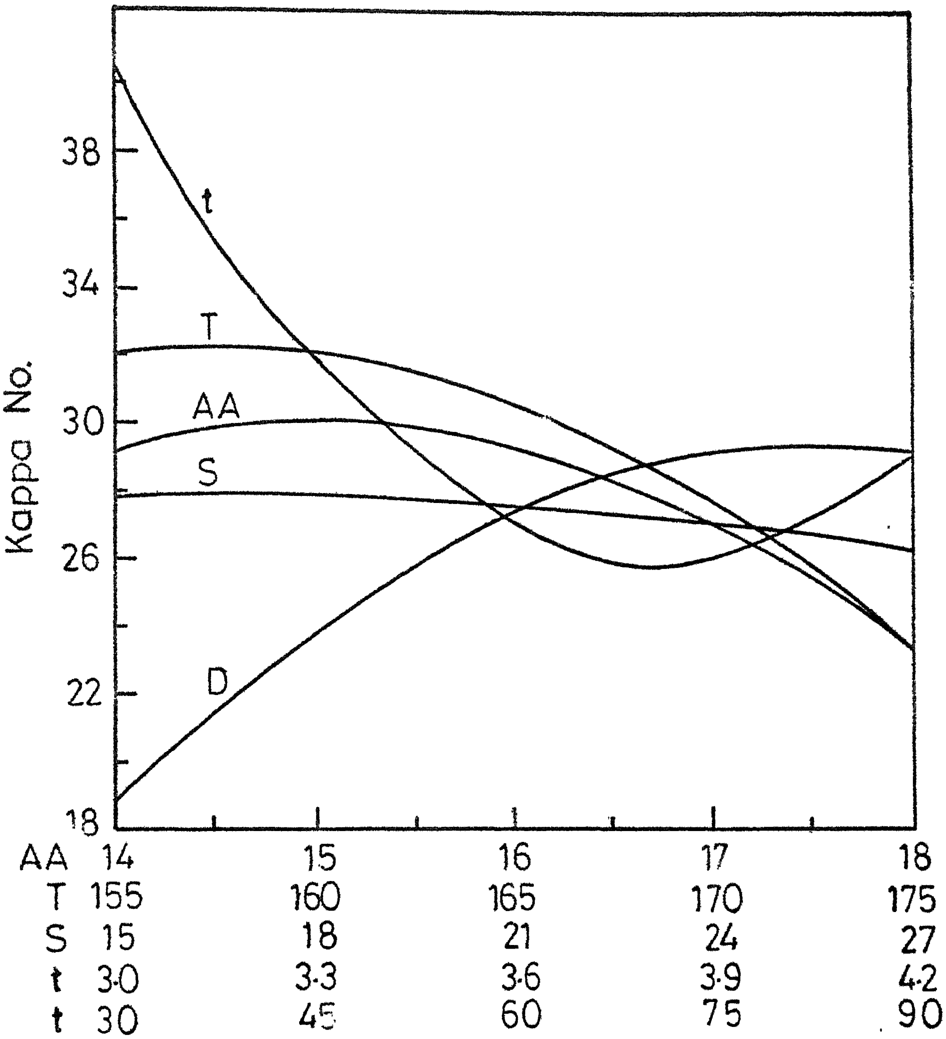


Fig. 5·3 - Univariate representation of response surface for Kappa number (eucalypt).

estimated optimum value of 57 min. It was observed in Figure 5.1 that pulp yield was independent of cooking time. The further increase in Kappa number observed during 70-90 min. may be attributed to probable condensation of residual pulp lignin with some of the hydrolyzed intermediates from the tannin like polyphenolic extractives of eucalypts. The influence of temperature and active alkali become significant at the higher levels. Sulfidity range (15-27 per cent) adopted appears to have virtually no effect on Kappa number. Increase in liquor-to-wood ratio to about 4:1 causes an increase in Kappa number.

The graphs in Figures 5.4, 5.5, and 5.6 show the variations in strength properties - burst index, tear index and tensile index respectively. It can be observed that the strength properties are reasonably uniform about the optimum pulping conditions, since the correlation coefficients obtained for the regression models adopted was only fair.

5.1.8.2 <u>Representation by Contour Plots</u>: The regression models for eucalypt pulping experiments have shown that chemical charge (x_1) and temperature (x_2) are the two most important pulping variables affecting pulp yield and properties. The response function (regression equation 5.3) based on 5 variables can be represented by a surface in a two-dimensional space formed by x_1 and x_2 with constant values

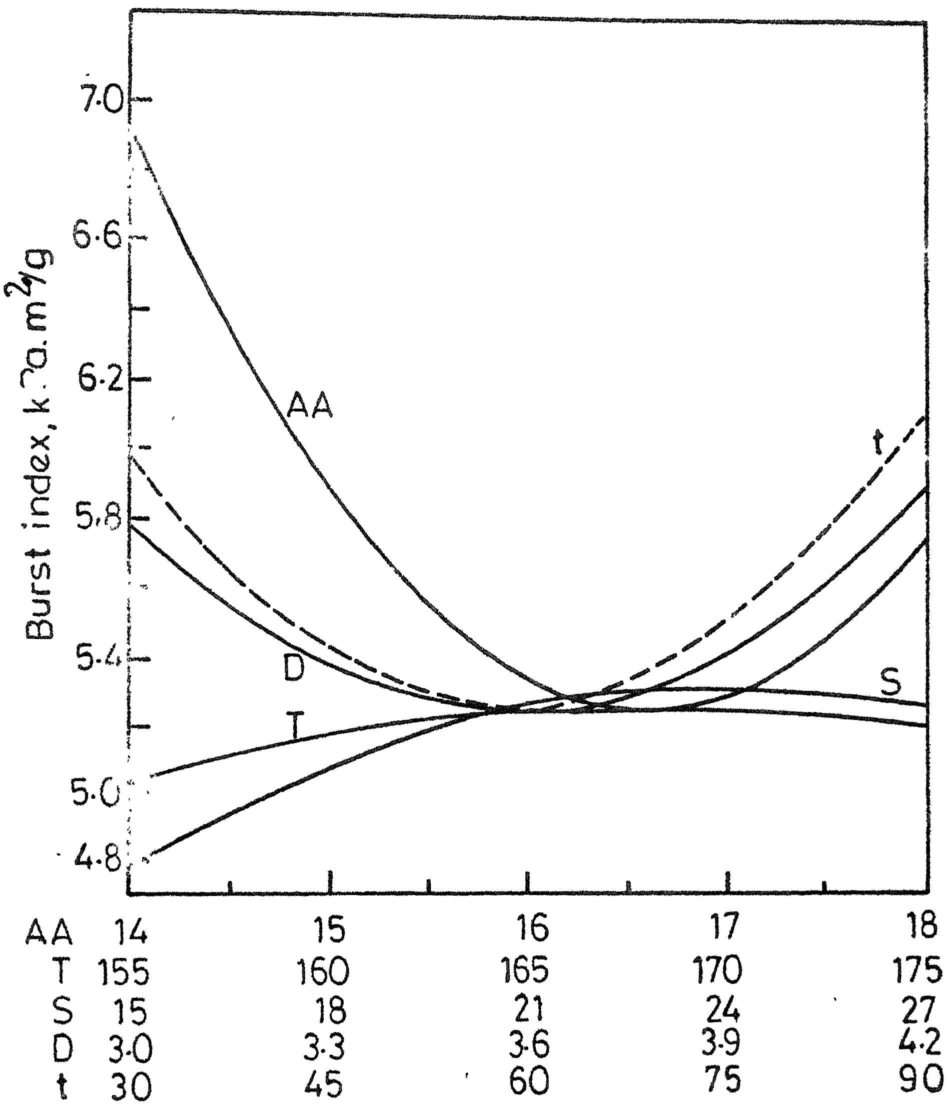


Fig. 5.4 - Univariate representation of response surface for burst index (eucalypt).

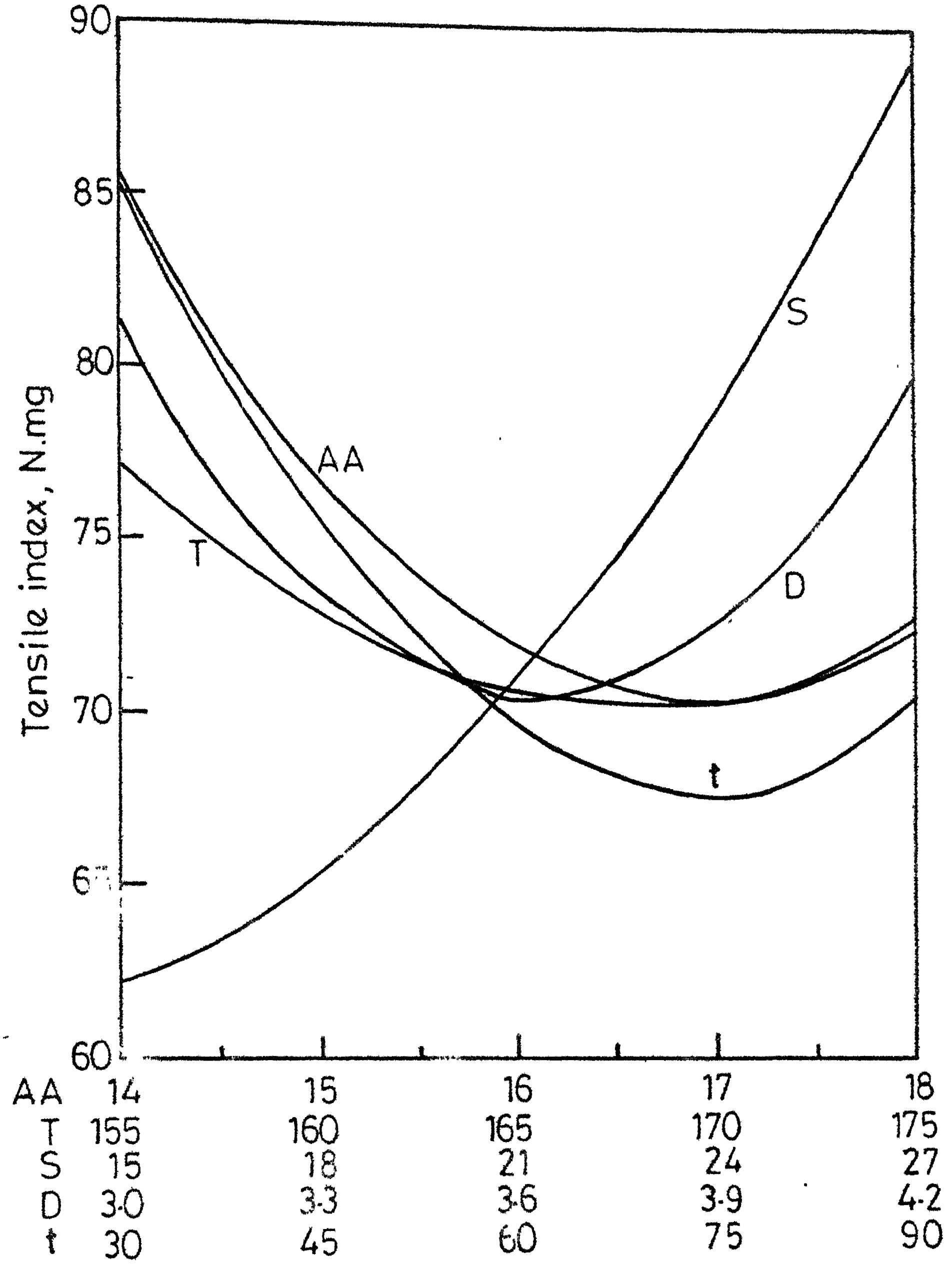


Fig. 5·6 – Univariate representation of response surface for tensile index (eucalypt).

selected for the three variables - x_3, x_4 and x_5. Such contour representations are very useful in depicting the variations in pulp properties caused by change in chemical charge and temperature.

Contour plot representation of pulp properties are reported in literature (Garceau et al., 1974; Mathur and Peterson, 1978; Chen et al., 1978). Garceau et al. (1974) have represented response surface of yield, Kappa number and ring crush in a 2-dimensional space as a function of active alkali charge and cooking time at maximum temperature in the high yield (55-61 per cent) kraft pulping of balsam fir chips. Mathur and Peterson (1978) have obtained second-order regression equation model (equation 5.3) for pulp yield in the poly-sulfide kraft pulping of sycamore (hardwood). The combined response of either of two variables (5 variables total) has been represented as a three-dimensional surface. The response surface for yield in hardwood softwood blend pulping by a two-dimensional surface is reported by Chen et al. (1978) with active alkali charge and hardwood fraction as variables.

Figures 5.7 - 5.11 show the response surfaces of pulp yield, Kappa number, burst index, tear index and tensile index respectively for variations in active alkali (14-18 per cent) and pulping temperature (155-175°C). The remaining three variables have been kept constant at the central point conditions.

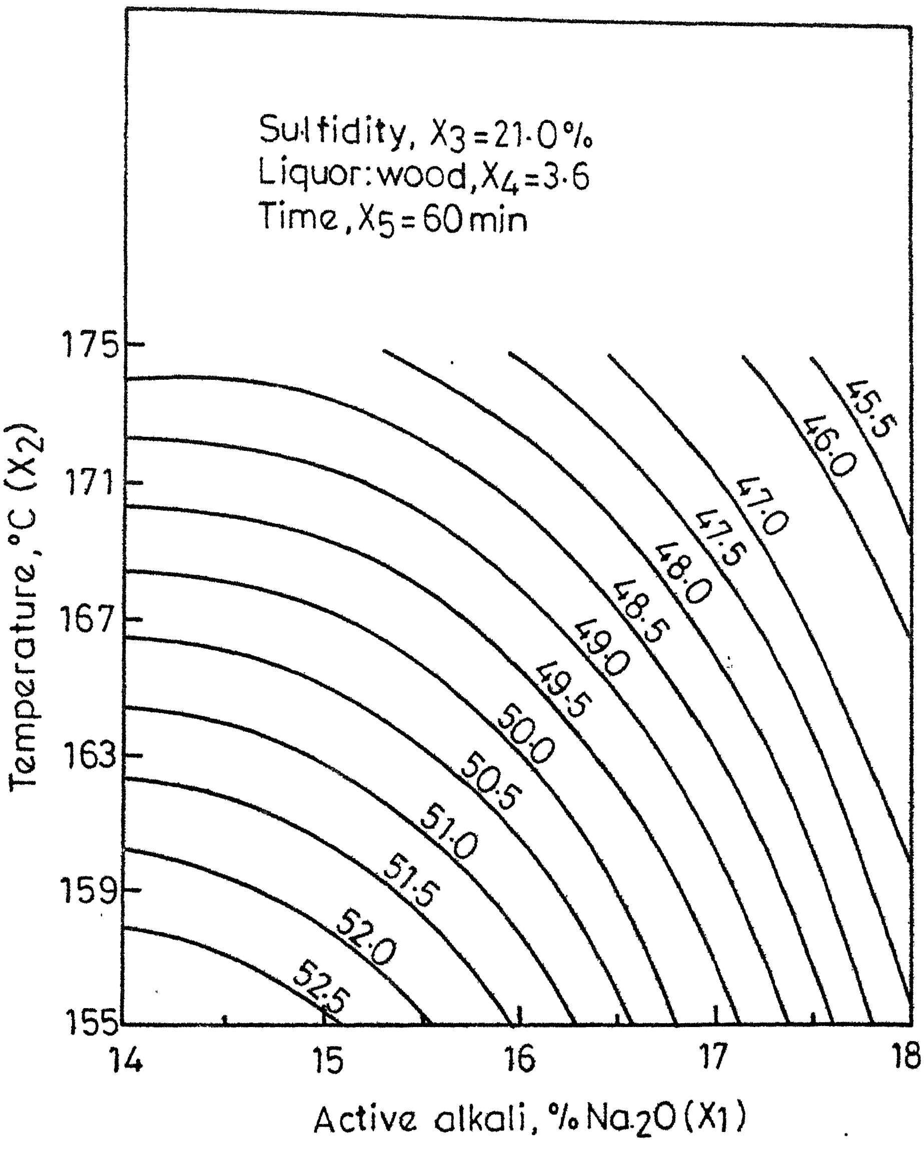


Fig. 5.7 - Response surface of pulp yield for various values of active alkali and temperature (eucalypt).

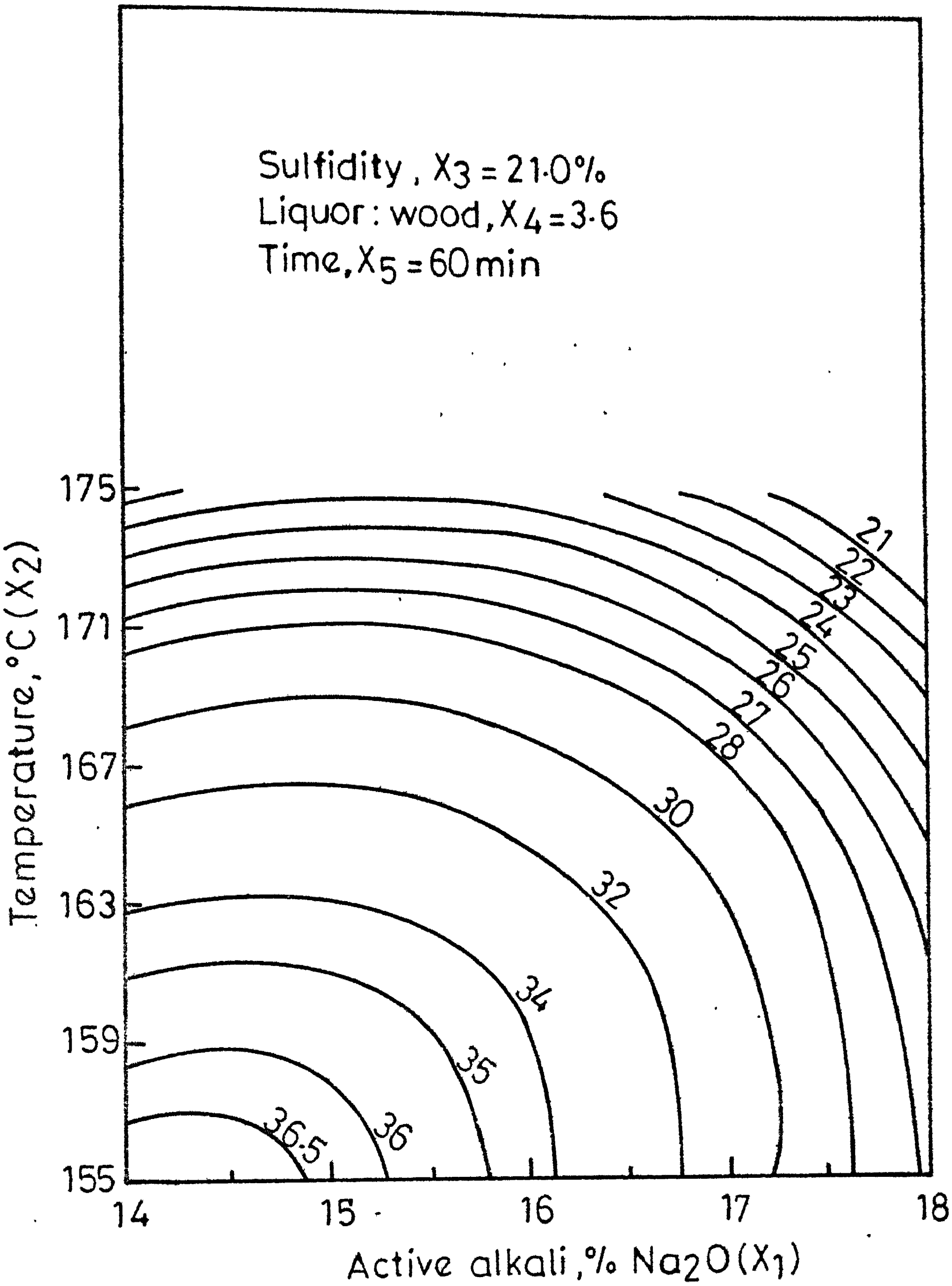


Fig. 5·8 – Response surface of Kappa number (eucalypt).

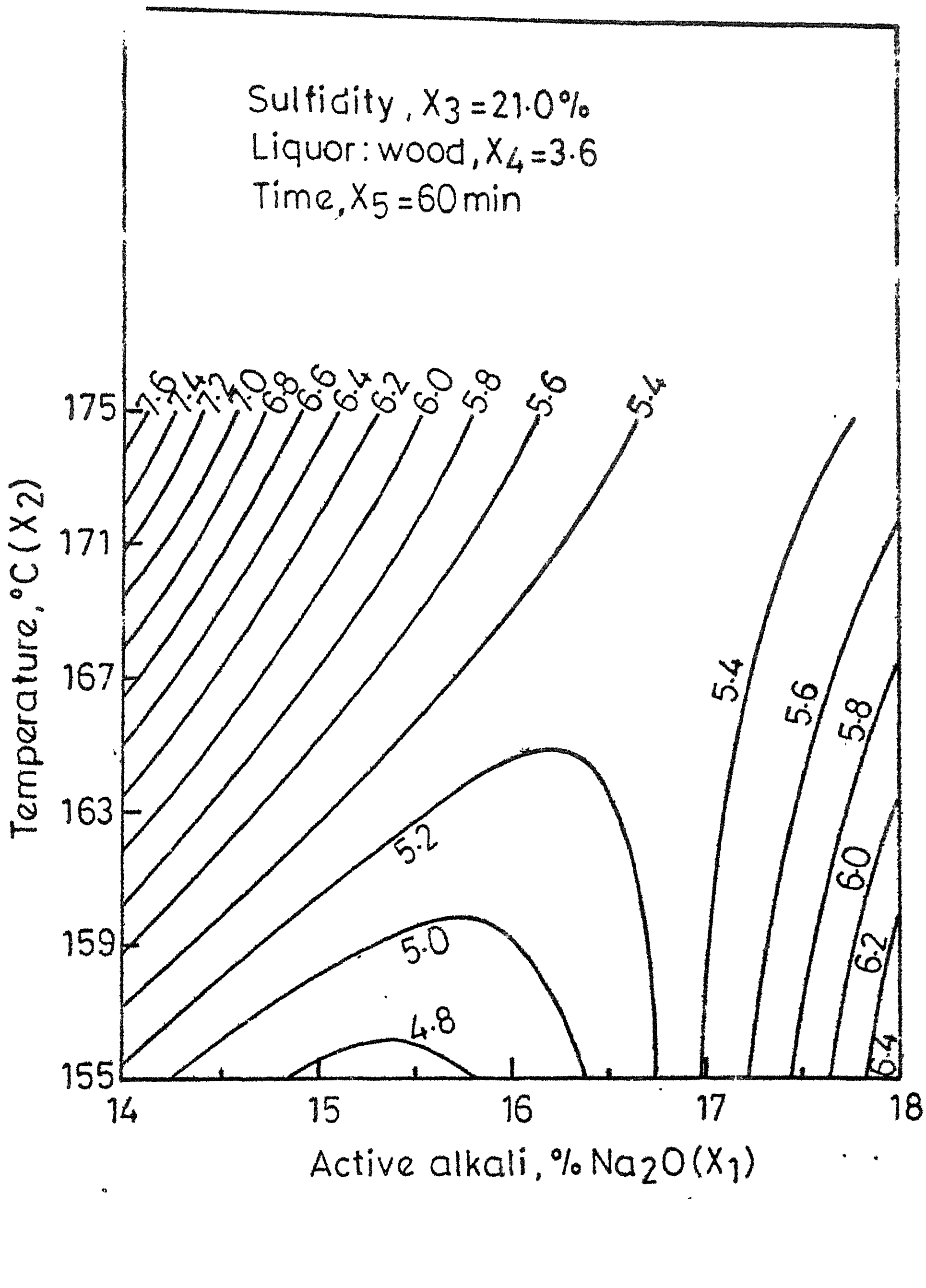
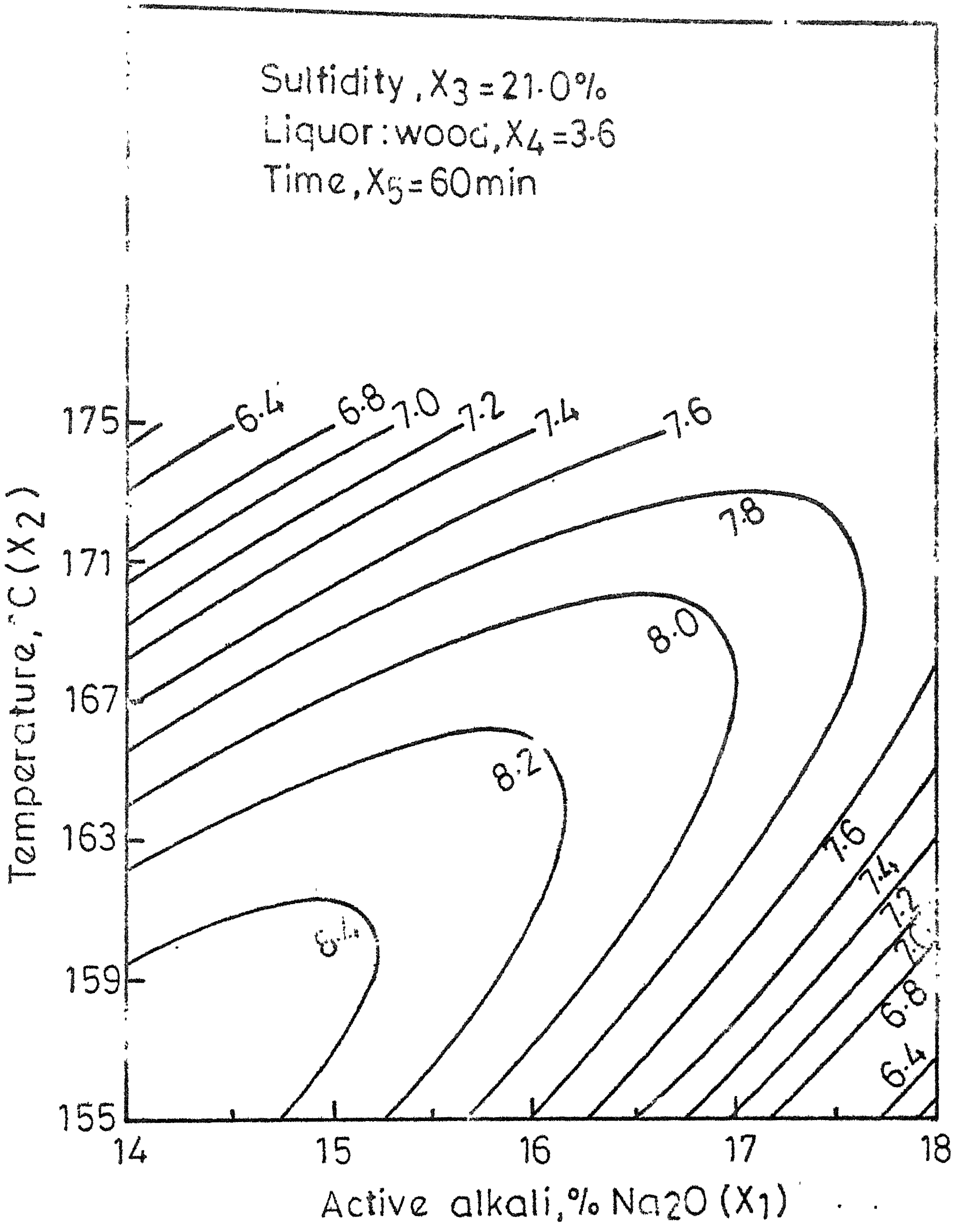


Fig. 5.9 - Response surface of burst index (eucalypt).



F . 5·10 - Response sur ace of tea index (eucalypt).

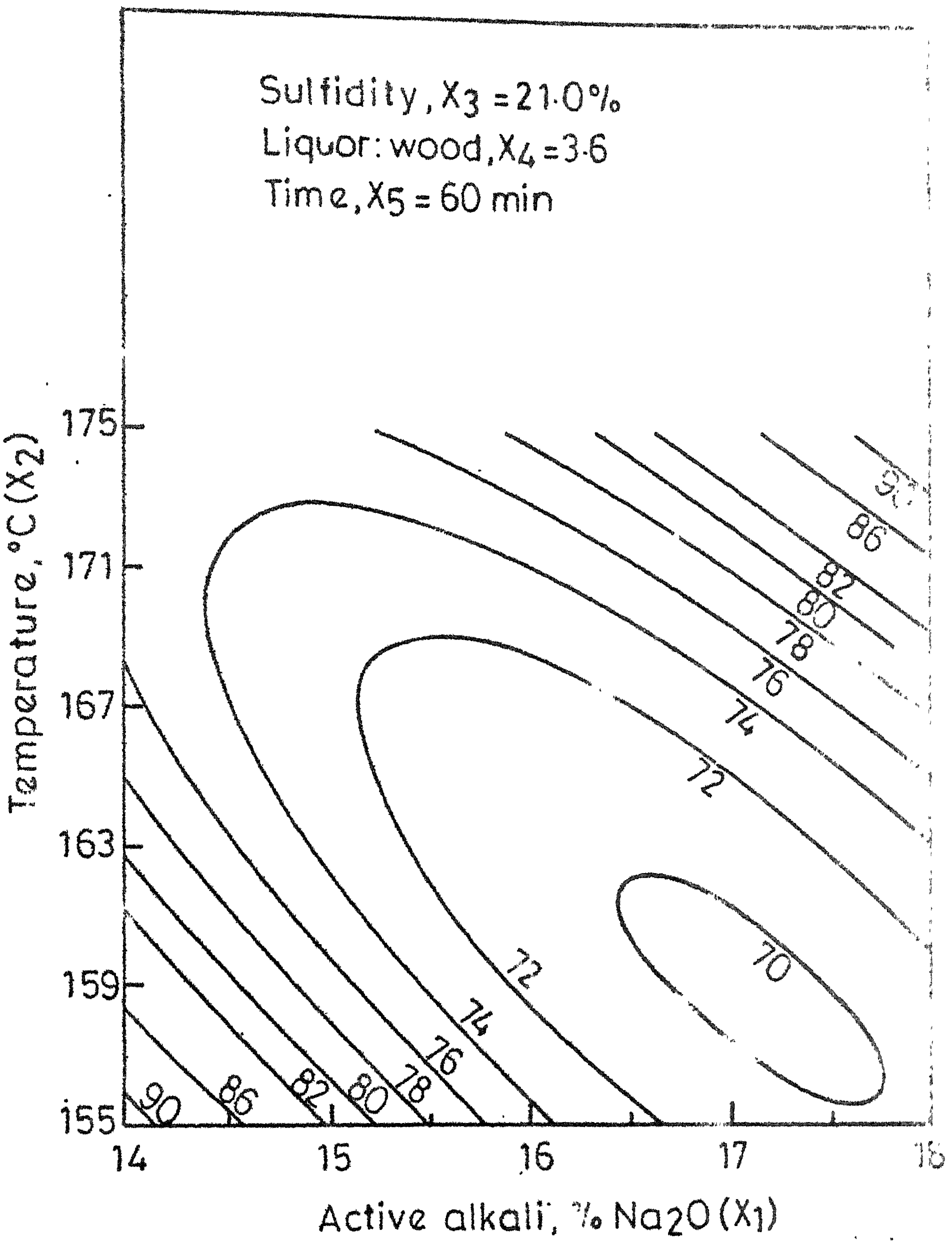


Fig. 5.11 - Response surface of tensile index (eucalypt).

Figure 5.7 shows the contour plots for different pulp yields (range = 45-53 per cent) and shows that various combinations of chemical charge and temperature can give the desired yield. The figure also showsthat pulp yield decreases faster with chemical charge at lower temperature levels. The effect of temperature is relatively less above active alkali level of 17 per cent. The above results are similar to the observations by Garceau et al. (1974) for the high yield pulping of balsam fir chips.

Response surface of Kappa number (range = 21-37) is shown in Figure 5.8. The figure shows that at a given temperature level, lower levels of chemical charge (14-16 pe cent) do not have any appreciable effect on Kappa number. Temperature significantly affects Kappa number specially at lower levels of chemical charge. Thus, at 15 per cent activ alkali charge, increase in temperature from 155° to 175°C decreases Kappa number from 36.5 to 24. Kappa number is not affected much by pulping temperature below 165°C for chemica charges of 16-18 per cent; at higher temperatures both the variables have an appreciable effect on Kappa number and an increase in either would tend to decrease the Kappa number.

Figure 5.9 shows the response surface for burst index which varies from 4.8 to 7.6. Burst index is at a minimum at lower levels of chemical charge and temperature and improves with delignification; a combination of low

chemical charge - high temperature or high chemical charge - low temperature is favoured according to the contour plots in Figure 5.9. The burst index increases for pulps cooked with 14-16 per cent active alkali at temperatures above 165°C as well as with 17-18 per cent active alkali at temperatures around 165°C.

However, in contrast to burst index, the response surface of tear index shows a maxima at lower left corner (Figure 5.10) corresponding to low levels of both the variables. Tear index usually increases with the progress of cooking and forms a rising ridge towards the origin of the contour plot.

The response surface of tensile index shown in Figure 5.11 suggests that both low chemical charge-temperature and high chemical charge-temperature combinations give better tensile index and has a minima around 17 per cent active alkali and 160°C.

The contour plots of strength properties have been obtained from regression equations with only fair (R^2=0.66 - 0.76) correlation coefficients and the results can be used as a guide to interprete the predicted behaviour. Pulping conditions recommended to obtain the maximum pulp yield and other properties are given below:

1. Unbleached grade kraft pulp in the Kappa number range = 27–33
   16 – 17.5% AA, 165–170°C
2. Good pulp yield (45–49 per cent): 16.5 – 18% AA, 165–170°C
3. Burst index (6 – 7.4): 14 – 15% AA, 169–173°C
4. Tear index (8.2 – 8.4): 14 – 16% AA, 157–161°C
5. Tensile index (75 – 90): 14 – 15% AA, 157–161°C
   or 17 – 18% AA, 167–173°C

From the above set of conditions, it can be observed that the various pulp properties require different pulping conditions and a compromise is necessary amongst pulp yield and the desirable/acceptable range of the remaining properties. Thus, at the central point conditions, the yield (49.7 per cent) is good with a Kappa number acceptable for unbleached paper grade pulp; tear index = 8.3, tensile index = 71 and burst index = 5.3, compared to the maximum values of 8.4, 90, and 7.0 respectively, obtainable over the range of the pulping variables studied.

5.2 KRAFT PULPING OF PINE

5.2.1 Exploratory Experiments:

Three independent pulping variables - chemical charge, temperature and time were studied in an exploratory two-level factorial design (8 experiments) to determine the effects on pulp yield and other properties. The range of the three variables was arbitrarily selected to correspond to the range used for eucalypts. The other pulping conditions were held constant at central point conditions of eucalypt pulping experiments and are shown in Table 5.26. Table 5.27 gives the pulping conditions and experimental results.

The data were analyzed using Yates's algorithm to determine the effects of the variables and for the analysis of the variance to determine the significance of the variables. A sample illustration of Yates' algorithm for a 2^3 factorial design for total pulp yield is given in Appendix III. Similar calculations were carried out for all the dependent variables and the results of the analyses are summarized in Table 5.28 showing the main effects and iteractions. Analysis of variance of the data has shown that only temperature is significant (at 95 per cent confidence level) for yield and active alkali consumption while temperature and time have a significant effect on Kappa number. Analysis of the experimental results leads to the following observations.

TABLE 5.26: KRAFT PULPING OF PINE

PULPING CONDITIONS FOR EXPLORATORY EXPERIMENTS

Variables	Symbol	Range (Levels) -1	+1
Chemical charge, % Na_2O	X_1	15	17
Temperature, °C	X_2	165	175
Time, min	X_5	60	90

Constants

Sulfidity, %	21
Liquor/wood ratio	3.6
Chip size, mm	18-25
Avg. thickness, mm	4.7
Time-to-temperature	90

Coded variables

x_1 = (chemical charge - 16)/1.0

x_2 = (Temperature - 170)/5.0

x_5 = (Time - 75)/15.0

TABLE 5.27: PULPING CONDITIONS AND EXPERIMENTAL RESULTS FOR THE EXPLORATORY PULPING EXPERIMENT WITH PINE CHIPS

Expt. no.	Pulping conditions			Experimental results			Kappa no.
	Chemical charge, % Na_2O	Temperature °C	Time, min	Total yield, %	BLS %	AA consumption, %	
P-1	15	165	60	50.33	18.94	11.47	89.46
P-2	17	165	60	49.18	20.03	11.84	97.69
P-3	15	175	60	47.66	21.81	11.81	73.58
P-4	17	175	60	46.81	23.53	12.18	78.10
P-5	15	165	90	48.54	20.28	11.36	74.47
P-6	17	165	90	48.93	22.00	11.38	73.73
P-7	15	175	90	48.49	22.05	12.13	62.70
P-8	17	175	90	46.87	22.42	12.31	66.17

TABLE 5.28: SUMMARY OF YATES'S ANALYSIS FOR THE MAIN EFFECTS AND INTERACTIONS – EXPLORATORY EXPERIMENTS

Main effects and interactions	Yield	BLS	AA consumption	Kappa no.
Average	48.41	21.39	11.81	76.99
Chemical charge	-0.93	1.24	0.24	3.87
Temperature	-1.91[a]	2.13[a]	0.60[a]	-13.70[a]
Chem.charge - temp.	-0.30	-0.19	0.04	0.14
Time	-0.41	0.60	-0.03	-15.44[a]
Chem.charge-time	0.32	-0.20	-0.14	-2.51
Temperature-time	0.86	-1.03	0.26	4.04
Chem.Charge-temp-time	-0.70	-0.48	0.04	1.97

[a]significant at 95 per cent confidence level.

1. All the three variables tend to decrease pulp yield in the order - temperature, chemical charge and time. Chemical charge although known to be an important factor affecting pulp yield has turned out to be statistically less significant than temperature; this suggests the need of increasing its range to a higher level.
2. Both the temperature and time tend to reduce Kappa number significantly. An increase in temperature in the range 165 - 175°C causes Kappa number to decrease by 13.7 units whereas increasing cooking time (60 - 90 min) decreases Kappa number by 15.4 units. The range of chemical charge (15-17 per cent) adopted is rather low to reflect a significant effect on the Kappa number; further, Kappa number range obtained in this study was also rather high (63-98). Consequently, the level and range of chemical charge is not adequate for satisfactory delignification.

The higher lignin content of the pine chips and the requirement for a lower Kappa number (30-45) suggests the need for a higher chemical charge. Kleppe (1970) has suggested 15-18 per cent active alkali charge (as Na_2O) for the kraft pulping of southern pines to obtain unbleached pulp with Kappa number = 30-60. Thus, while the exploratory

temperature range studied appears to be adequate, the ranges of chemical charge and time must be increased for the subsequent experiments.

5.2.2 Effect of Time-to-Temperature:

The interacting effect of time-to-temperature (60, 120 min) and temperature (165, 175°C) was studied by a simple factorial design and the results are analyzed by Yates's method, similar to the earlier study for eucalypt chips (section 5.1.1. Pulping conditions and results are summarized in Tables 5.29 and 5.30 respectively.

The estimates of the effects show that pulping temperature is the most significant variable affecting both the total yield and screened yield. The effect of increase in time-to-temperature (60, 120 min) is secondary and only marginally improves the screened yield. The interaction effect of the two variables is small compared to the main effects unlike the earlier observation for eucalypt pulping.

An increase in temperature (165, 175°C) reduces Kappa number by 27 points and is the most significant variable; time-to-temperature has no significant effect on Kappa number. The results of this analysis show that slow heating (60 min vs 120 min) has only a nominal effect on pine pulping even though it was observed to be advantageous in the case of eucalypt pulping. Nevertheless, an average value (90 min) appears to be an appropriate choice for heating period and has been selected for all the subsequent experiments of this study.

TABLE 5.29: KRAFT PULPING OF PINE
EFFECT OF TIME-TO-TEMPERATURE
PULPING VARIABLES AND CONSTANTS

Variables	Symbol	Range (Levels) -1	+1	Incremental change
Temperature, °C	x_2	165	175	+10
Time-to-temperature, min	x_7	60	120	+60

Constants:

Chemical charge, % Na_2O	17.5
Sulfidity, %	25
Liquor/wood ratio	3.75
Time-at-temperature, min	80
Chip size, mm	-18+12
Average chip thickness, mm	4.0 (s.d. = 1.5)

Coded variables

x_2 = (Temperature - 170)/5.0

x_7 = (Time-to-temperature - 90)/30.0

TABLE 5.30: KRAFT PULPING OF PINE

EFFECT OF TIME-TO-TEMPERATURE AND TEMPERATURE

A. Pulping Conditions and Experimental Results

Expt. no.	Pulping conditions		Pulping Results				
	Temp. °C	TTT min.	Total yield %	Screened yield, %	BLS	AA consumption	Kappa no.
P-11	165	60	51.10	48.54	21.11	12.28	63.7
P-12	165	120	50.08	49.39	21.21	12.16	59.7
P-13	175	60	45.90	44.48	23.55	12.87	34.3
P-14	175	120	45.56	45.03	24.57	13.29	34.5

B. Calculation of Main Effects and Interactions by Yates's Method

Factors and interaction	Main effects				
	Total yield	screened yield	BLS	AA consumption	Kappa no.
Average	48.16	46.86	22.61	12.65	48.05
Time-to-temp.	-0.68	0.70	0.56	0.16	-1.90
Temperature	-4.86	-4.21	2.90	0.87	-27.30
TTT x Temp. interaction	0.34	-0.15	0.46	0.28	2.1

5.2.3 Influence of Chip Size (Thickness)

Mill run pine chips were manually screened and hand sorted to remove irregular/defective chips and knots. Three chip fractions were obtained - (-12 + 6 mm), (-18 + 12 mm) and (-25 + 18 mm) with average thickness of 2.8 mm, 4.0 mm and 4.7 mm (25-30 per cent deviation) respectively. The length (5-35 mm) and thickness (2.0 - 6.0 mm) of the hand sorted chips were in the desired range for the kraft pulping of pine chips.

The influence of chip thickness, chemical charge, and temperature was studied with a two-level factorial design. The range of pulping variables is shown in Table 5.31, and pulping conditions and experimental results are given in Table 5.32.

Analysis of the data by Yates's algorithm is summarize in Table 5.33, and the significant effects have been marked with 'a' in the table. The following conclusions are based on the above analyses.

1. Temperature has a pronounced effect on pulp yield and Kappa number compared to chemical charge and chip size. A 10°C rise in pulping temperature (165-175°C) decreases total yield by 4.8 per cent. Increase in chemical charge (16-19 per cent) decreases pulp yield by 2.9 per cent whereas chip thickness appears to have no appreciable effect on total yield.

TABLE 5.31: KRAFT PULPING OF PINE
EFFECT OF CHIP THICKNESS
PULPING VARIABLES AND CONSTANTS

Variables	Symbol	Range (Levels) -1	+1	Incremental change
Chemical charge, % Na_2O	x_1	16	19	+3
Temperature, °C	x_2	165	175	+10
Chip size, mm	x_6	-12+6	-25+18	+12
Average chip thickness, mm		2.82	4.73	-
Standard deviation		0.76	1.32	-

Constants

Sulfidity,%	25
Liquor/wood ratio	3.75
Time-at-temperature, min	80
Time-to-temperature, min	90

Coded variables

x_1 = (chemical charge - 17.5)/1.5

x_2 = (temperature - 170)/5.0

x_6 = (average chip size - 15)/6.0

TABLE 5.32: KRAFT PULPING OF PINE

EFFECT OF CHIP THICKNESS

PULPING CONDITIONS AND EXPERIMENTAL RESULTS

Expt. no.	Pulping conditions			Experimental results			
	Chemical charge %	Temperature °C	Chip thickness, mm	Total yield %	Screened yield %	AA consumption %	Kappa no.
P-21	16	165	2.8	50.3	50.2	11.7	60.6
P-22	19	165	2.8	47.6	47.5	12.1	55.6
P-23	16	175	2.8	44.4	44.3	12.8	36.7
P-24	19	175	2.8	42.3	42.3	13.4	28.4
P-25	16	165	4.7	50.2	45.7	11.3	67.1
P-26	19	165	4.7	46.6	45.5	12.3	63.8
P-27	16	175	4.7	45.9	42.9	12.2	41.1
P-28	19	175	4.7	42.8	41.6	13.5	27.4

TABLE 5.33: KRAFT PULPING OF PINE
EFFECT OF CHIP THICKNESS
MAIN AND INTERACTION EFFECTS OF VARIABLES BY YATES'S METHOD

Main and interaction effects	Total yield %	Screened yield %	Rejects %	AA consumption %	Kappa no.
Average	46.27	45.00	1.27	12.40	47.59
Chem. charge	-2.89[a]	-1.55	-1.34	0.81[a]	-7.5[illegible]
Temperature	-4.84[a]	-4.46[a]	-0.38	1.11[a]	-28.3[illegible]
Chem.-temp.	0.29	-0.07	-0.43	0.10	3.4[illegible]
Chip thickness	0.19	-2.16[a]	2.35[a]	-0.19	4.53
Chem.-thickness	-0.49	0.77	-1.26	0.28	-0.93
Temp.-thickness	0.73	1.07	-0.34	-0.06	-2.83
Chem.-temp.-thickness	-0.02	-0.45	0.43	0.03	-1.73

[a]significant at 95 per cent confidence level

2. Reduction in chip thickness reduced screen rejects to give higher screened pulp yield. Thus, reducing chip thickness from 4.7 mm (-25 +18 mm fraction) to 2.8 mm (-12+6 mm fraction) increased screened yield by 2.2 per cent. Increase in chemical charge also reduces screen rejects. Interaction effect between temperature and chip thickness shows that thin chips cooked at lower temperatures will give higher screened yield. These results are in agreement with the results reported in previous studies (Hartler and Onisko, 1962; Borlew and Miller, 1970).
3. Increase in chemical charge or temperature increases active alkali consumption. Increase in chip thickness in the range studied has no appreciable effect on active alkali consumption.
4. Temperature is the most significant variable affecting Kappa number. An increase in temperature from 165 to 175°C reduces Kappa number by 28.4 units similar to the observation in the previous section (5.2.2). A 3 per cent increase in chemical charge (16-19 per cent) reduces Kappa number by 7.6 units. Increase in chip thickness (in the range studied) increased Kappa number by 4.5 units as expected.

It can be concluded from the above observations that thin chips pulped at lower temperature levels increase screened pulp yield. Borlew and Miller (1970) have reported 3 mm thick chips as optimum for yield and uniformity. Pine chips (fraction -18+12 mm) with an average thickness of 4.0 mm was selected for the subsequent experiments.

5.2.4 Fractional Factorial Design:

Among the seven independent pulping variables in the kraft digester system, the effects of time-to-temperature (section 5.2.2) and the influence of chip size (section 5.2.3) were studied separately and appropriate constant values were selected for the subsequent experiments. The heating period was maintained constant at 90 min and fractionated chips (-18 +12 mm, average thickness -4.0 mm) were used for all the experiments. Consequently, the effects of the remaining five independent variables - chemical charge, temperature, sulfidity, liquor-to-wood ratio and pulping time were studied using a half replicate of a 2^5 factorial design, with six replicate experiments at the central point conditions.

5.2.4.1 Regression Analysis of Experimental Data: The range of the pulping variables studied are given in Table 5.34. Details of the pulping conditions and the experimental results are given in Table 5.35. Runs P-31 to P-46 belong to the half-fraction factorial design and runs P-47 to P-52 are the replicate runs at central point conditions. The average

TABLE 5.34: KRAFT PULPING OF PINE

PULPING VARIABLES AND CONSTANTS

2^5 FACTORIAL DESIGN WITH HALF REPLICATE AND REPEATED EXPERIMENTS AT THE CENTRAL POINT

Variables	Symbol	Range (Levels) -1	0	+1	Incremental change
Chemical charge, % Na_2O	x_1	16.0	17.5	19.0	+1.5
Temperature, °C	x_2	165	170	175	+5.0
Sulfidity, %	x_3	20	25	30	+5.0
Liquor/wood ratio	x_4	3.5	3.75	4.0	+0.25
Time, min	x_5	60	80	100	+20

Constants

Chip size, mm	-18+12
Avg. chip thickness, mm	4.0
Time-to-temperature, min	90

Coded variables

x_1 = (chemical charge -17.5)/1.5

x_2 = (temperature - 170)/5.0

x_3 = (sulfidity -25)/5.0

x_4 = (liquor/wood ratio - 3.75)/0.25

x_5 = (time -80)/20

TABLE 5.35: KRAFT PULPING OF PINE
5 INDEPENDENT VARIABLES

A. Pulping Conditions

Expt. no.	Chemical charge % X_1	Temperature °C X_2	Time min X_5	Sulfidity % X_3	Liquor-to-wood ratio X_4
P-31	16	165	60	20	4.0
P-32	19	165	60	20	3.5
P-33	16	175	60	20	3.5
P-34	19	175	60	20	4.0
P-35	16	165	100	20	3.5
P-36	19	165	100	20	4.0
P-37	16	175	100	20	4.0
P-38	19	175	100	20	3.5
P-39	16	165	60	30	3.5
P-40	19	165	60	30	4.0
P-41	16	175	60	30	4.0
P-42	19	175	60	30	3.5
P-43	16	165	100	30	4.0
P-44	19	165	100	30	3.5
P-45	16	175	100	30	3.5
P-46	19	175	100	30	4.0
P-47	17.5	170	80	25	3.75
P-48	17.5	170	80	25	3.75
P-49	17.5	170	80	25	3.75
P-50	17.5	170	80	25	3.75
P-51	17.5	170	80	25	3.75
P-52	17.5	170	80	25	3.75

Table 5.35 contd

B. Experimental Results

Expt. no.	Total yield %	Screened yield %	Black liquor solids %	AA consumption %	Kappa number
P-31	45.38	43.02	17.75	10.89	73.8
P-32	41.20	40.74	22.82	11.34	53.7
P-33	44.46	43.52	24.43	12.02	46.9
P-34	43.29	42.88	22.13	12.63	40.4
P-35	47.83	46.39	22.60	11.42	70.3
P-36	45.00	44.47	21.87	12.19	48.3
P-37	43.67	42.53	19.03	12.73	50.8
P-38	41.50	41.36	20.87	12.32	30.4
P-39	50.28	47.76	21.43	11.35	72.8
P-40	48.72	47.63	20.62	11.39	59.6
P-41	47.55	45.52	17.96	11.41	50.5
P-42	44.81	44.14	22.51	13.65	32.6
P-43	48.20	46.46	17.23	12.35	59.6
P-44	46.78	46.70	23.80	12.58	31.3
P-45	43.66	43.13	24.39	12.18	37.7
P-46	43.09	43.01	22.15	13.42	31.3
P-47	47.17	46.49	23.51	12.70	53.2
P-48	48.38	47.69	22.83	12.45	44.4
P-49	44.87	43.76	22.99	11.94	53.6
P-50	45.56	44.93	23.92	12.00	43.2
P-51	45.60	44.18	22.29	13.16	43.2
P-52	45.56	44.64	23.50	11.73	57.4

Table 5.35 contd

C. Strength Properties

Expt. no.	Burst index kPa m^2g^{-1}	Tear index mN m^2g^{-1}	Tensile index N m g^{-1}
P-31	6.39	12.51	74.57
P-32	6.51	12.43	79.13
P-33	6.06	9.38	86.59
P-34	5.98	12.51	88.93
P-35	5.68	12.32	75.97
P-36	6.42	13.07	78.67
P-37	6.86	12.51	86.97
P-38	5.67	11.38	80.98
P-39	6.26	12.69	85.96
P-40	6.68	12.07	73.56
P-41	6.77	12.40	83.02
P-42	6.46	13.50	76.20
P-43	6.51	13.30	73.27
P-44	7.83	14.07	80.43
P-45	6.99	11.41	89.27
P-46	6.80	11.81	89.50
P-47	6.89	11.93	89.00
P-48	6.37	15.48	75.79
P-49	7.32	10.82	75.89
P-50	7.33	13.98	83.73
P-51	6.53	14.30	74.72
P-52	6.50	14.08	75.42

values and the standard deviation in the data obtained at the central point conditions are given in Table 5.36. Standard deviations for all the dependent variables can be regarded as satisfactory, although the values for Kappa number (5.0), burst index (0.43) and tear index (1.72) are rather high. The latter can be attributed to the heterogeneous morphological and chemical character of the pine chips.

The range of dependent variables studied and the total variation observed in the dependent variables are given in Table 5.37. A comparison of the latter with the estimated experimental error shows that the responses observed can be regarded to be statistically significant and all the pulping variables would significantly affect the pulping results.

The experimental data were correlated with a polynomial regression equation consisting of linear and interaction terms, equation (5.4):

$$y = b_o \sum_{i=1}^{5} b_i x_i + \sum_{i<j}^{5} b_{ij} x_i x_j \qquad (5.4)$$

The sixteen parameters were estimated by the method of least squares and the results are summarized in Table 5.38. A typical example of a regression equation for total yield is given by equation (5.5),

TABLE 5.36: KRAFT PULPING OF PINE
MEAN AND STANDARD DEVIATION OF PULPING RESULTS
FOR EXPERIMENTS AT CENTRAL POINT CONDITIONS

Expt. no.	Total yield %	Screened yield %	AA consumption %	Black liquor solids %	Kappa no.	Burst index, kPA m^2g^{-1}	Tear index, mN m^2g^{-1}	Tensile index, N m g^{-1}
P-47	47.17	46.49	12.70	23.51	53.17	6.89	11.93	89.00
P-48	48.38	47.69	12.45	22.83	44.40	6.37	15.48	75.79
P-49	44.87	43.76	11.94	22.99	53.60	7.32	10.82	75.89
P-50	45.56	44.93	12.00	23.92	43.20	7.33	13.98	83.73
P-51	45.60	44.18	13.16	22.29	43.20	6.53	14.30	74.72
P-52	45.56	44.64	11.73	23.50	57.40	6.50	14.08	75.79
Mean	46.19	45.28	12.33	23.17	49.16	6.82	13.43	79.15
s.d.	1.314	1.505	0.540	0.584	6.283	0.425	1.717	5.845

TABLE 5.37: KRAFT PULPING OF PINE
RANGE OF PULPING VARIABLES EVALUATED

Dependent variable (Response)	Range	Total variation	Standard deviation
Total yield, %	41.2 - 50.3	9.1	1.314
Screened yield, %	40.7 - 47.8	7.1	1.505
Black liquor solids,%	17.23- 24.43	7.2	0.584
AA consumption,%	10.9 - 13.7	2.8	0.540
Kappa number	30.4 - 74.8	44.4	6.283
Burst index, kPa $m^2 g^{-1}$	5.6 - 7.9	2.3	0.425
Tear index, mN $m^2 g^{-1}$	9.3 - 15.5	6.2	1.717
Tensile index, N m g^{-1}	73.2 - 89.3	16.1	5.845

TABLE 5.38: KRAFT PULPING OF PINE

MATHEMATICAL MODEL

Para-meters	Coefficients							
	Total yield	Screened yield	Black liquor solids	AA cons-umption	Kappa number	Burst index	Tear index	Tensile index
b_o	45.571	44.588	21.846	12.175	49.618	6.582	12.634	80.779
b_1	- 1.040	- 0.461	0.748	0.322	- 8.706	0.052	0.270	- 0.514
b_2	- 1.335	- 1.062	0.335	0.427	- 9.581	-0.043	-0.473	3.744
b_3	1.297	1.217	-0.087	0.174	- 2.731	0.296	0.321	- 0.038
b_4	0.273	0.110	-1.506	0.008	2.131	0.059	0.188	- 0.378
b_5	- 0.372	-0.072	0.425	0.282	- 4.131	0.103	0.149	0.444
b_{12}	0.208	0.047	-0.516	0.137	2.306	-0.237	0.168	- 0.766
b_{13}	0.254	0.290	0.261	0.146	0.481	0.103	-0.064	- 0.965
b_{14}	0.452	0.522	1.102	-0.041	1.818	-0.133	-0.428	2.118
b_{15}	1.297	0.092	-0.066	-0.095	-1.490	0.033	-0.171	1.026
b_{23}	-0.524	-0.528	-0.156	-0.054	0.681	0.011	0.096	-0.648
b_{24}	0.122	0.111	0.140	-0.006	1.044	0.094	0.258	2.300
b_{25}	-0.651	-0.684	-0.216	-0.165	1.606	0.028	-0.234	1.054
b_{34}	-0.020	0.001	-0.265	-0.157	1.193	-0.157	-0.449	-1.186
b_{35}	-0.831	-0.646	0.488	0.059	-2.818	0.142	-0.158	1.273

Table 5.38 contd

Para-meters	Coefficients							
	Total yield	Screened yield	Black liquor solids	AA consum-ption	Kappa no.	Burst index	Tear index	Tensile index
b_{45}	-0.250	-0.246	0.085	0.263	-0.156	-0.007	0.001	0.598
R^2	0.899	0.823	0.829	0.347	0.942	0.754	0.458	0.716

$$y = b_o + \sum_{i=1}^{5} b_i x_i + \sum_{i<j}^{5} b_{ij} x_i x_j \qquad (5.4)$$

Total pulp yield, per cent

$$Y_t = 45.57 - 1.04x_1 - 1.33x_2 + 1.29x_3 + 0.27x_4 - 0.37x_5 + 0.20x_1x_2 + 0.25x_1x_3 + 0.45x_1x_4 + 1.29x_1x_5 - 0.52x_2x_3 + 0.12x_2x_4 - 0.65x_2x_5 - 0.02x_3x_4 - 0.83x_3x_5 - 0.25x_4x_5 \quad (5.5)$$

$(R^2 = 0.90)$

Good correlation was obtained for total pulp yield, screened yield, Kappa number, black liquor solids and active alkali consumption with $R^2 = 0.899$, 0.823, 0.942, 0.629 and 0.884 respectively. Correlation was satisfactory for burst index ($R^2 = 0.754$) and tensile index ($R^2 = 0.72$) and was poor for tear index ($R^2 = 0.46$). The poor correlation observed in strength property data are similar to the results obtained earlier for eucalypt pulps. It can be attributed to the inevitable factors relating to pulp post-digestion treatment steps besides the abnormal fiber dimensions of the heterogeneous pine chips used.

Fiber length and wall thickness have an important influence on the strength properties of the paper produced. Long fibers are more flexible while thin-walled fibers tend to collapse on drying to form flat ribbons. These flattened ribbons offer greater opportunity for fiber-fiber contacts than thick-walled fibers and hence produce paper of high bursting and tensile strength. Long fibers in general give better strength properties provided they are thin-walled (flexible). The benefits of long fibers are offset by the

coarsness (wall thickness) of the fibers. Tear index is directly proportional to the slenderness ratio (length/diameter) of the fibers. At low levels of pulp refining, thick-walled fibers produce a relatively bulky paper, which is low in tensile and bursting strength but has high tearing resistance (Clark, 1978).

The average fiber length (5.0 mm) of the pine pulps studied is higher than the average length reported for normal pines (3.5 mm); the diameter is comparable to the normal pines (32-43 µm). However, the fiber wall thickness (10.1 - 15.1 µm) is about four times higher than the wall thickness of normal pines (2.4 - 3.8 µm). Large variations in the fiber dimensions have resulted in a pulp of heterogeneous strength behaviour. Thick walled fibers have given lower burst index (5.6 - 7.9) compared to normal pines (6-10). The tensile index (73-89) is also on the lower side compared to normal pines (80-125). The tear index (9.3 - 15.5) obtained is comparable to normal kraft pulp.

The polynomial regression equation (5.4) gives the best estimates of yield, Kappa number and strength properties for the kraft pulping of pine chips and has been used in subsequent studies.

5.2.5 Miscellaneous Models:

Miscellaneous kraft pulping models were tried with the data of the pine pulping experiments similar to eucalypts

and the correlations were observed to be less satisfactory. The results of the various trials are summarized below:

1. Regression model fitted with effective alkali as a variable gave essentially the same correlation coefficient for yield and Kappa number (similar to eucalypts).

2. Regression model using H-factor in the second-order model (equation 5.4 plus square term for H-factor) gave good correlation for Kappa number (R^2=0.89) but was poor for yield.

3. Sulfidity and liquor-to-wood ratio were also included in Hatton (1973) model (model 10, Table 2.2) and active alkali instead of effective alkali was used. The model gave a good fit for Kappa number and the correlation was very poor for yield.

$$K = 225.47 - 15.39[(AA)^{0.48} \log (H)] - 0.546(S) + 8.524(D)$$

$$R^2 = 0.83$$

4. The logarithmic models proposed by Chari (1973), and Lin et al. (1978) modified with the inclusion of sulfidity were satisfactory for Kappa number with R^2 = 0.85 but poor for yield.

$$K = 675834 \frac{(D)^{0.884}}{(AA)^{2.095}(H)^{0.513}(S)^{0.299}}$$

However, the value of the constant (675834) is very large compared to the range given by Lin et al. (1978) for seven hardwoods (1835-3976) and the exponent of the variables are also quite different (Table 2.2).

The results of the above analysis shows that the second-order model (equation 5.4) correlating the effects of the five pulping variables would give a satisfactory representations of the digester responses similar to the observations for eucalypts.

5.2.6 Effect of Pulping Variables:

An examination of the mathematical model for pulp yield (equation 5.5) shows that the absolute effect of each independent variable is not clearly distinguishable because of the presence of interaction terms in the regression equation. However, their effects can be visualized by comparing the magnitudes of the coefficients of the linear terms. The effects of individual variables on yield and Kappa number is discussed below. A satisfactory interpretation of the effects of the variables on the strength properties is rendered difficult by the low correlation coefficients and the heterogeneous physico-chemical characteristics of the pulp fibers obtained with the abnormal pine chips used in this work.

5.2.6.1 Pulp Yield: Equation (5.5) shows that sulfidity is the most important variable influencing screened yield.

Temperature and chemical charge are observed to be the next important pulping variables. Earlier works reported in the literature on the pulping of softwoods (Hinrichs, 1967; Bailey et al., 1969; Hatton et al, 1971; Garceau et al., 1974; Hatton, 1976) shows that chemical charge is the most important pulping variable and temperature comes only next to it. This may be attributed due to the fact that in the previous studies, a wider range and higher level of chemical charge (12-22 per cent effective alkali) have been used. The lower chemical charge used in this work was prompted by a bias towards the level used for the pulping of eucalypt chips.

Sulfidity (20-30 per cent) increases the screened pulp yield similar to the observations of Bray and Morton (Rydholm, 1965; p.624) and Hinrichs (1969) above 20 per cent sulfidity at constant active alkali. Kleppe (1970) reports that the influence of sulfidity in the range (15-40 per cent) is much more in softwoods (pine) compared to hardwoods and is in agreement with the results of this study. An increase in temperature or chemical charge reduces pulp yield. Time and liquor-to-wood ratio have shown a rather small contribution to screened pulp yield. Significant interactions are also observed between chemical charge-liquor-to-wood ratio, temperature-sulfidity, temperature-time and sulfidity-time.

5.2.6.2 Kappa Number: Pulping temperature has the most significant influence on Kappa number as shown by the magnitude

of the coefficient b_2 in equation (5.4), (Table 5.38). The other important pulping variables in the order of decreasing influence are chemical charge and time; an increase in either or both decreases Kappa number. Increase in sulfidity appears to decrease Kappa number while liquor-to-wood ratio causes a small increase in Kappa number. The effects of sulfidity and liquor-to-wood ratio are small compared to the effects of temperature, chemical charge and time. Significant interactions are observed between chemical charge-temperature, chemical-charge-liquor:wood ratio, and sulfidity-time. The trends are in general agreement with the related studies with normal pine chips.

5.2.7 Recommended Pulping Conditions:

The regression equations for the kraft pulping of pine, equation (5.4) were used to determine the optimum pulping conditions to give maximum yield and/or strength properties and the Constrained Rosenbrock method was used for optimization similar to the earlier analysis with eucalypts.

Several trial combinations of any two/three constraints from among yield, Kappa number, and strength properties were used for the optimization study. The results of all the trials are summarized in Table 5.39. The objective was to maximize the response shown in column (2) subject to the constraints in column (3). The optimum pulping conditions and the estimates of the maximum value of the desired objective

TABLE 5.39: OPTIMIZATION OF KRAFT PULPING OF PINE

Serial no.	Objective function	Constraints and range	Optimum conditions: Chemical charge %	Temp., °C	Sulfidity %	Liquor/ wood	Time min	Pulp properties at optimum
1.	Yield	Kappa = 35 - 60 BI = 6.4 - 7.8	16.1	168	30.0	3.50	62.8	Yield = 49.37 Kappa = 59.0 BI = 6.47
2.	BI	Yield = 43 - 48 Kappa = 30 - 60	19.0	166	29.8	3.53	96.6	Yield = 46.6 Kappa = 35.1 BI = 7.75
3.	BI	Yield = 42 - 48 Kappa = 30 - 60 TI = 12.7 - 14.3	19.0	167	30.0	3.50	92.9	Yield = 46.2 Kappa = 40.4 BI = 7.68 TI = 14.12
4.	TI	Yield = 43 - 48 Kappa = 40 - 55 BI = 6.8 - 8.4	19.0	166	29.7	3.53	78.1	Yield = 46.7 Kappa = 44.6 BI = 7.53 TI = 14.19
5.	TI	Yield = 43 - 48 Kappa = 40 - 55 BI = 6.8 - 8.4	19.0	167	28.9	3.50	85.8	Yield = 46.0 Kappa = 40.4 BI = 7.46 TI = 14.00

Kappa - Kappa number BI = Burst index TI = Tear index

and other pulp properties obtainable are also given in the table.

For example, in trial 1, the objective was to maximize pulp yield, subject to the constraints on Kappa number and burst index in the range 35-60 and 6.4-7.8 respectively. The maximum yield was 49.37 per cent for the optimum conditions shown in the table; the Kappa number and burst index of the pulp were 59.0 and 6.47 respectively. In trial 3, three constraints were introduced (yield: 43-48, Kappa number: 30-60; tear index: 12.7-14.3) and the pulping conditions determined for maximum burst index; the pulp had the following properties - yield = 46.2, Kappa number = 40.4, burst index = 7.68 and tear index = 14.12. In trials 4 and 5 tear index was maximized subject to constraints on yield, Kappa number and burst index for the ranges shown in the table. These two trials differ in the initialization values of the variables for the optimization program; lower levels of the variables for trial 4 and higher levels for trial 5. The results are quite similar and confirms the fact that the optimization method is working well with this system. The estimates of the pulping conditions for maximum burst index (trial 3) are close to the estimates for maximum tear index (trials 4 and 5) with a slight variation in pulping time.

Pulping experiments (P-71, P-72, P-73) were conducted in triplicate adopting the conditions of trial 3 and the

results are summarized in Table 5.40, which also gives the estimates based on 'Constrained Rosenbrock Method'. The results show very good agreement for pulp yield (98 per cent) and the agreement is within 4 per cent for tear index and tensile index and 14 per cent for Kappa number and burst index.

The results of the various trials for the location of the optimum pulping conditions show that the predicted values of chemical charge, sulfidity and time are near the upper level while temperature and liquor-to-wood ratio are at the lower level of the experimental region. These predicted conditions corresponding to the extremes of the experimental region cannot be said to represent the true optimum. A true or global optimum could have been obtained if a wider range of the pulping variables were studied, especially for chemical charge, sulfidity and liquor-to-wood ratio. Consequently, the conditions recommended in Table 5.40 may be regarded as the best conditions corresponding to maximum burst index/tear index obtainable with the imposed constraints on pulp properties over the experimental region of this study.

5.2.8 Representation of the Response Surface:

5.2.8.1 Univariate Representation: Univariate representation of the response surface for screened yield and Kappa number during the kraft pulping of pine was obtained by the regression equation models (Table 5.38) while keeping all variables at

TABLE 5.40: KRAFT PULPING OF PINE

BEST PULPING CONDITIONS AND PREDICTED RESPONSES

COMPARISON WITH THE ACTUAL PULPING RESULTS

Variables and responses	Best pulping conditions				
	Estimates	P-71	P-72	P-73	Mean (Exptl.)
Constant conditions					
Chip size range, mm	-18+12	-18+12	-18+12	-18+12	-
Avg. thickness, mm	4.0	4.0	4.0	4.0	-
Time-to-temperature, min	90	90	90	90	-
Pulping variables					
Chemical charge, % Na_2O	19	19	19	19	-
Temperature, °C	167	167	167	167	-
Sulfidity, %	30	30	30	30	-
Liquor-to-wood ratio	3.5	3.5	3.5	3.5	-
Time, min	93	93	93	93	-
Responses					
Pulp yield, %	46.2	45.7	45.3	44.9	45.3
Black liquor solids, %	24.0	21.2	21.5	21.4	21.4
AA consumption, %	12.7	13.1	12.6	-	12.9
Kappa number	40.4	53.1	53.0	31.6	45.9
Burst index, $kPa.m^2g^{-1}$	7.68	7.02	6.70	5.93	6.55
Tear index $mN\ m^2g^{-1}$	14.12	15.13	14.62	14.09	14.61
Tensile index, $N\ m\ g^{-1}$	79.63	76.89	77.43	75.91	76.74
Folding endurance	-	1007	1300	1154	1154

the best predetermined conditions and varying only a single variable over the experimental region, as was done earlier for eucalypts.

Figure 5.12 shows the effect of change in cooking conditions on screened yield. Temperature has the maximum influence on yield. Chemical charge appears to have less effect compared to temperature. Increase in sulfidity or liquor-to-wood ratio has a positive effect on yield and pulping time has essentially no effect.

Figure 5.13 shows the effect of pulping variables on Kappa number of the pulp. Kappa number decreases with an increase in the level of all the variables except liquor-to-wood ratio. Kappa number appears to be most sensitive to chemical charge at the best predicted conditions since its slope is maximum. All the variables show a linear effect on pulp Kappa number.

Both the screened pulp yield and kappa number have shown linear dependence on the pulping variables in the range studied unlike the behaviour obtained for eucalypt pulping. This may be attributed to the fact that pulping variables were probably studied over a narrower range and no maxima/ minima are observed in the curves. With a wider range, true (global) optimum conditions could have been located.

5.2.8.2 Representation by Contour Plots: The regression models for pine pulping experiments have shown that chemical charge

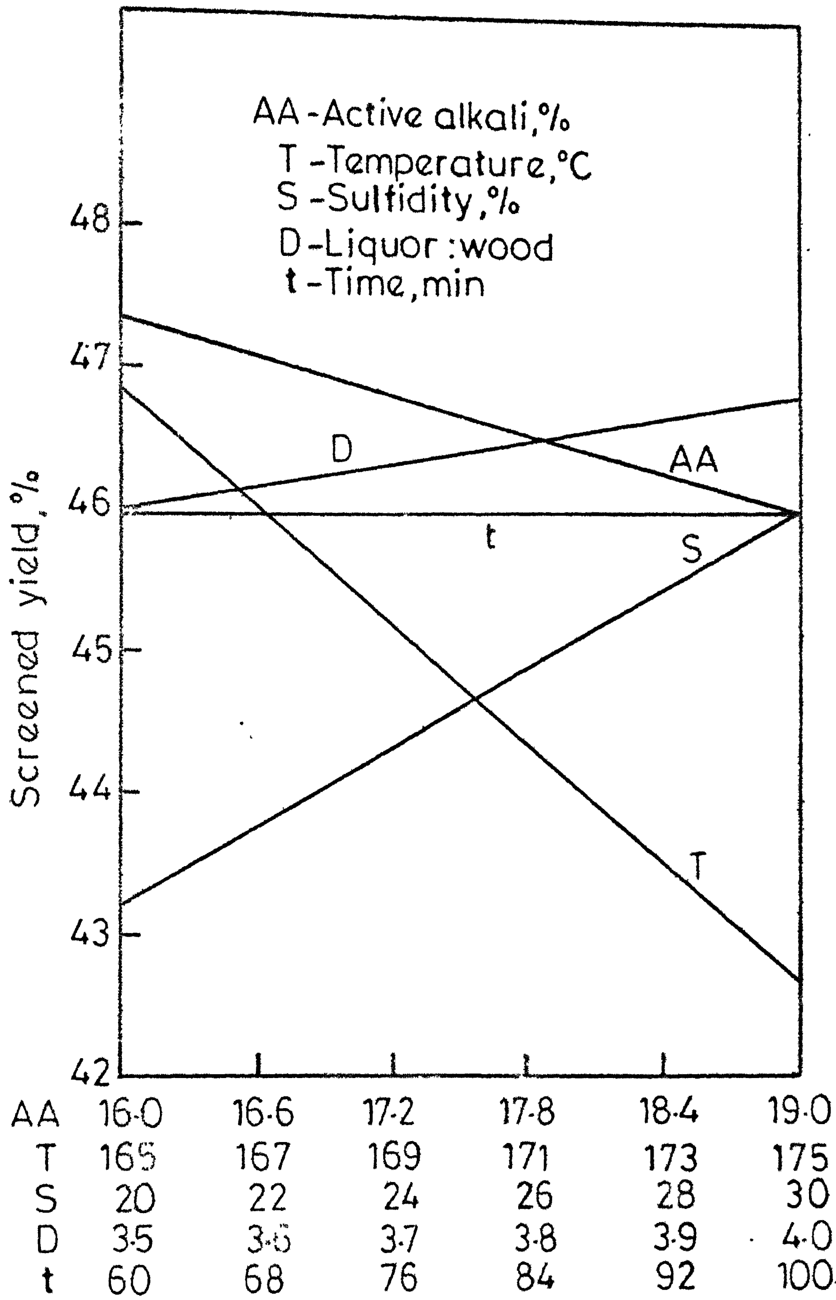


Fig.5·12 - Univariate representation of response surface for screened yield (pine).

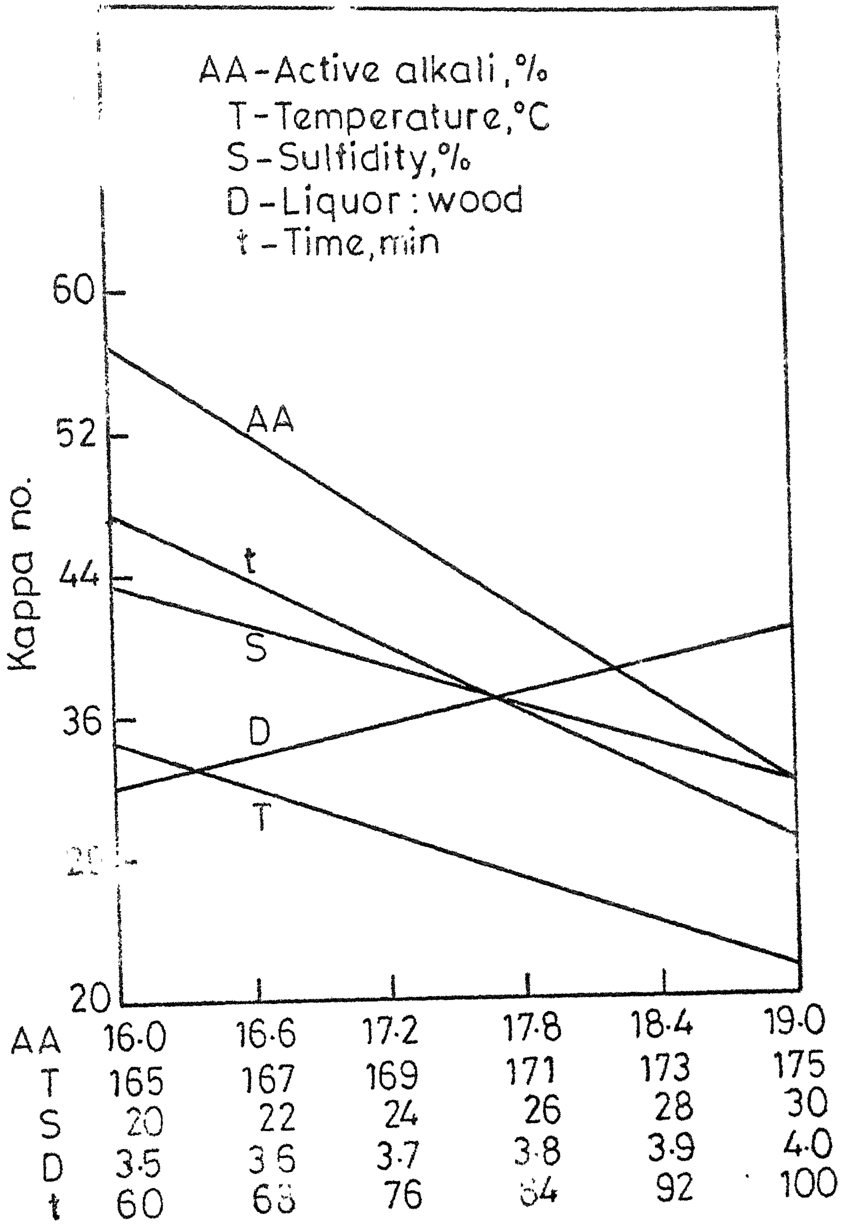


Fig. 5·13- Univariate representation of the response surface for Kappa number (pine).

and temperature are the two most important pulping variables affecting pulp yield and properties. The response surface equation (5.4) can be represented by a surface in a two-dimensional space by keeping three variables (x_3, x_4, x_5) constant at the optimum value and varying only the chemical charge and temperature.

Figures 5.14 and 5.15 show response surfaces of screened pulp yield and Kappa number for the experimental range of active alkali (16-19 per cent Na_2O) and temperature (165-175°C) with sulfidity = 30 per cent, liquor:wood = 3.5, and pulping time = 93 min.

Contour lines of constant yield (range = 42.5 - 48.0 per cent) shows the various possible combinations of chemical charge and temperature, Figure 5.14. The contour lines are observed to be parallel in the range studied similar to the results reported by **Garceau et al.**(1974). The response surface of Kappa number (range = 18-59) in Figure 5.15 shows the strong influence of both the chemical charge and temperature. These plots give the following ranges of active alkali and temperature for the desired yield and Kappa number of unbleached pine kraft pulp.

Pulp yield (45-47 per cent): 17-19 per cent AA, 166-171°C

Kappa number(35-50) : 17-18 per cent AA, 166-172°C

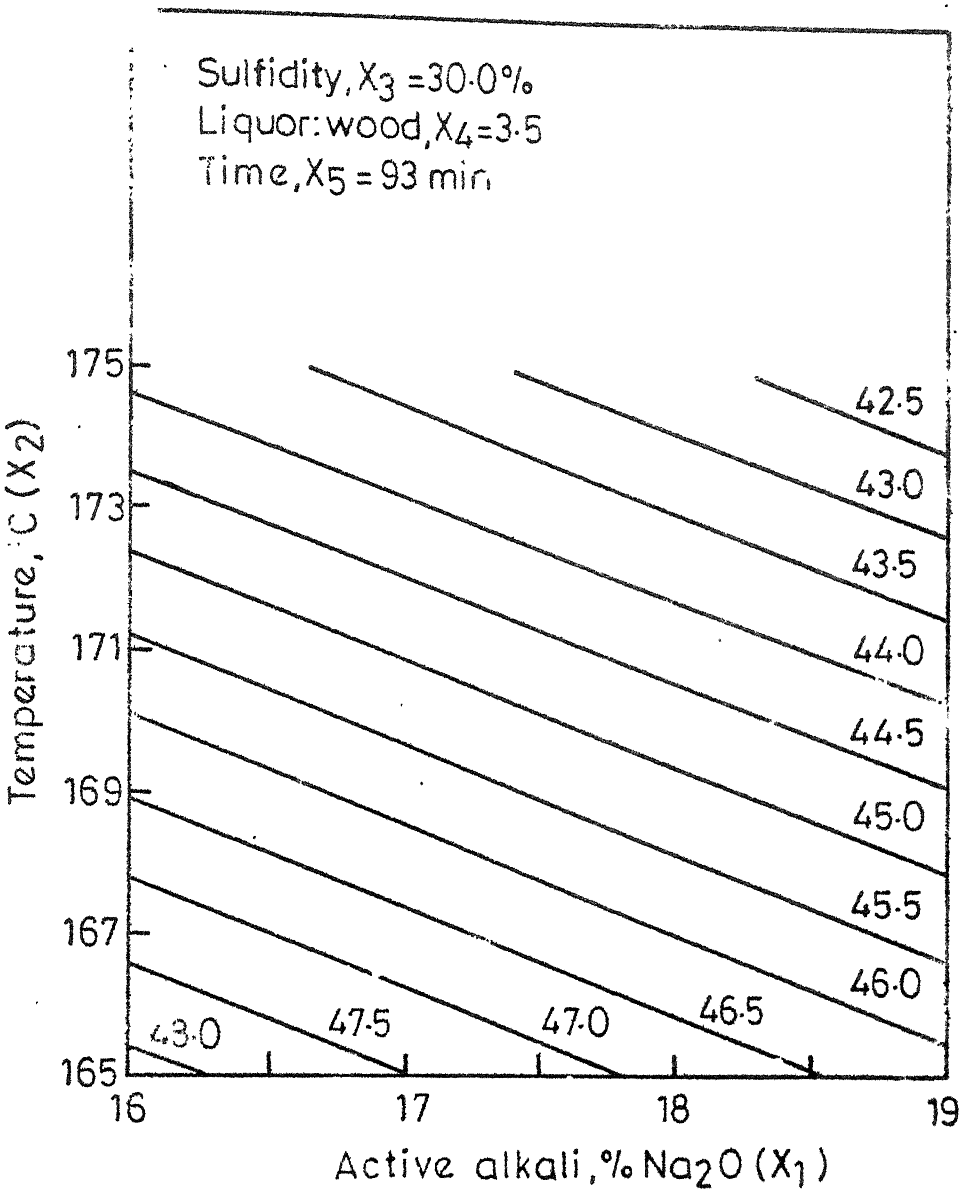


Fig. 5-14–Response surface of screened yield for various values of active alkali and temperature (pine).

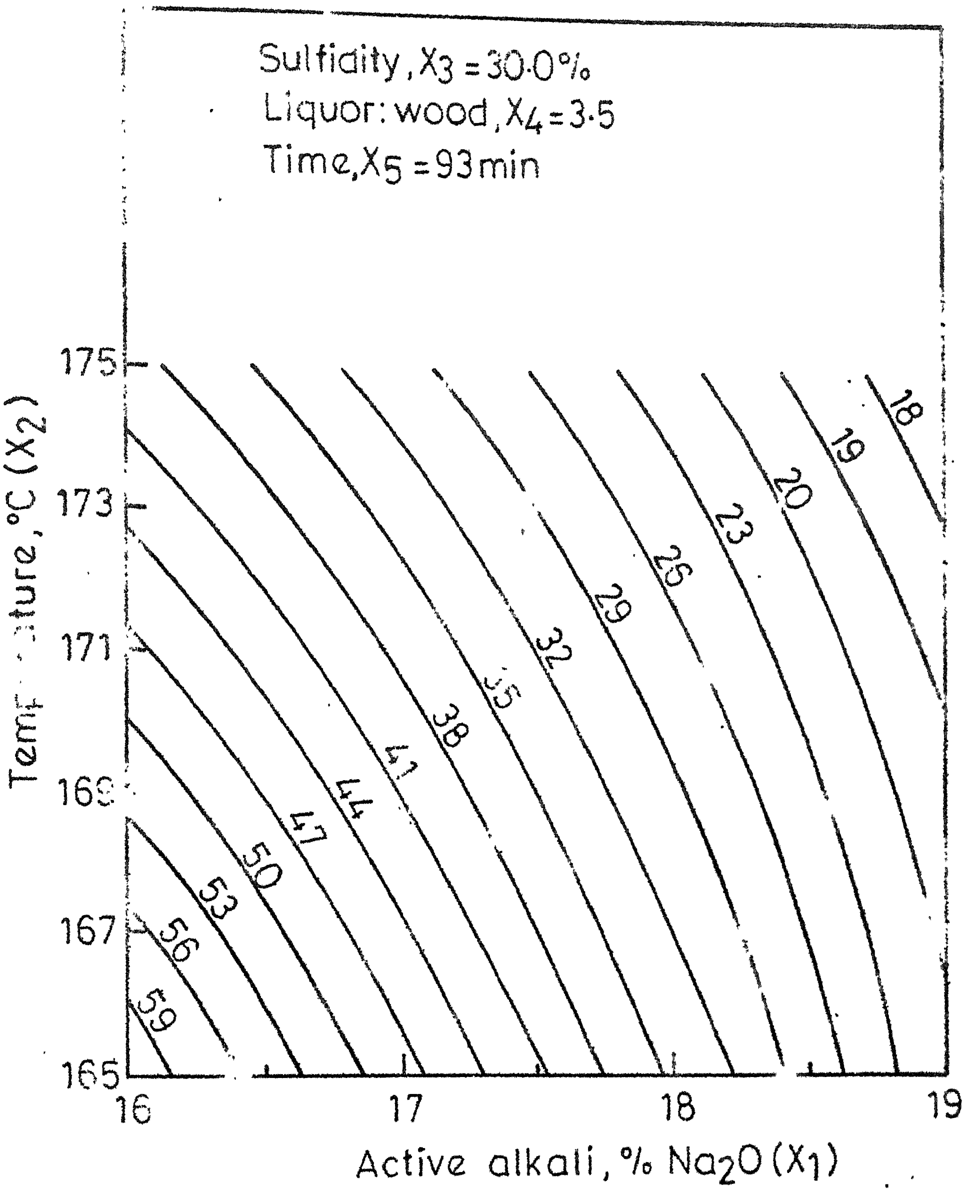


Fig. 5.15 - Response surface of kappa number for vari[illegible]us values of active alkali and temperature (pine).

5.3 KRAFT PULPING OF EUCALYPT AND PINE CHIP BLENDS

The optimum conditions for pulping of eucalypts (section 5.1.7) and the best conditions recommended for the pulping of pine (section 5.2.7) according to this study are summarized below:

Variable	Eucalypt	Pine
Chemical charge, per cent	16.8	19.0
Temperature, °C	170	167
Sulfidity, per cent	20.7	30
Liquor-to-wood ratio	3.63	3.5
Time, min.	57	93

The higher chemical charge, sulfidity and pulping time for pine are necessitated by the higher lignin content of pine (33.1 per cent) compared to eucalypts (28.5 per cent) based on proximate analysis of extractive free wood meal samples. The α-cellulose content of the eucalypt was higher (49.8 per cent) compared to pine (46.3 per cent) and the former also contained an appreciable quantity (about one-sixth) of alkali soluble polyphenolic extraneous components. The eucalypt chips contained 17 per cent pentosan compared to about 9 per cent in pine. The above factors would lead to a higher yield of eucalypt kraft pulp compared to pine.

Eucalypt chips cooked at the optimum pulping conditions give 47.5 per cent yield at a Kappa number of 27.2 with the

following strength properties: burst index = 5.3, tear index = 8.1, tensile index = 75.6 and folding endurance = 540. These strength properties are comparable to the results reported by Phillips et al. (1967) and Higgins (1970) for Australian native eucalypts. The best conditions for the pulping of pine chips have given pulp yield of 46.2 per cent at a Kappa number of 40.4 with the following strength properties: burst index = 7.7, tear index = 14.1, tensile index = 79.6 and folding endurance = 1154. A comparison of the strength properties of the above pulps shows that the long fibers of pine kraft pulps (average length - 5.0 mm) give superior tearing strength and folding endurance. The short fibers of eucalypt pulps (average length - 0.63 mm) would give good sheet formation with a smooth surface and the tensile index is comparable to the pine pulps.

Eucalypt pulps are also reported to have low wet web strength, drainage properties and runnability on the paper machine (Higgins, 1969, 1970). Thus it will be necessary to improve the sheet forming behaviour and strength properties of the eucalypt pulps. This study deals with the latter aspect by considering suitable blending procedures with pine which would also improve the performance on the paper machine. The pulp of the desired strength properties can be obtained by either pulp blends or by using chip blends

for pulping. Eucalypt and pine pulps can be blended in various proportions and beaten to the desired freeness level for strength development or the eucalypt and pine pulps can be beaten separately and subsequently blended prior to sheet formation. The composite pulp from pulping binary chip blends can also be beaten to obtain the necessary strength characteristics.

5.3.1 Studies on Softwood/Hardwood Blends:

Published literature is available on both the above aspects of blending - pulp blends, and chip blends. Phillips et al. (1967) have studied the blending of various proportions (0-100 per cent) of separately beaten eucalypt (E. diversicolor) and pine (P. pinaster) kraft pulps and reported considerable improvements in the tearing resistance and folding endurance of the former with no major effects on the bursting and tensile strengths. It was also observed that good tearing strength was obtained for the pulp blends using lightly beaten pine kraft pulp. Colley (1973) has studied blends of eucalypt (E. tetrodonta) and pine (P. radiata) pulps refined to different fressness levels in a PFI mill. The strength properties of the pulp blends can be estimated as the weighted average value of the properties of the component pulps (Peckham and May, 1959; Brecht, 1963; Almin and Ruvo, 1967; Colley, 1973; Nordman, 1973); the linear addition gave somewhat lower estimates for tearing strength

(Arlov, 1963; Bovin and Teder, 1971; Colley, 1973). Nordman (1973) has shown the validity of the weighted average method for the estimation of the bursting strength of linerboard grade pulp blends using pine and 30 per cent hardwood (Oak/hickory/gum) pulp. It was also observed that for maximum utilization of hardwood pulps at optimum strength properties, the hardwood pulp should be refined as much as possible while pine pulp should be beaten light.

Investigations by Hunt and Hatton (1976), Hatton (1977), Hannah and Swann (1981) and Chen et al. (1978) relate to the pulping of binary chip blends using small proportions of hardwood chips alongwith the main digester furnish consisting of softwood chips. Hunt and Hatton (1976) have reported the kraft pulping behaviour of single softwood chips (white spruce, western hemlock, or jack pine) blended with 20 per cent of single hardwood chips (red alder, yellow birch or trembling aspen). It was observed that the chip mixtures pulp faster to a given permanganate number and give high pulp yield with strength properties comparable to softwood pulps. Chen et al. (1978) also have reported similar findings for the yield and strength characteristics of kraft pulps obtained from blends of aspen/spruce chips (0-100 per cent). De Oliviera et al.(1981) have studied kraft pulping of chip blends of pine (0-100 per cent) and eucalypt (P. strobus var. chiapensis and E. urophylla) and reported the

improvements in the strength characteristics with the proportion of pine chips at different levels of refining. Goel and Ayroud (1980) have studied kraft pulping of binary/ ternary chip blends of pine and hardwood (maple/poplar) using statistical experimental designs and correlated the strength properties of the pulps on ternary diagrams representing digester chip proportions. The objective of the above studies has been the conservation of softwood resources and increase pulp production.

This study deals with the reverse aspect of the addition of a small quantity of softwood (pine) to the main digester furnish of eucalypt, to improve the strength properties of the latter. The diversities in optimum pulping conditions for eucalypt and pine observed earlier would necessitate separate pulping with subsequent blending of the pulps to obtain the desired strength requirements. However, for the small proportion of pine (up to 30 per cent) envisaged in this study it is considered appropriate to pulp chip blends at 165°C with an intermediate chemical charge (18 per cent) and other conditions close to the optimum for eucalypt pulping.

The methodology of the work is to assess the improvement in the strength of the eucalypt pulps resulting from the use of a small proportion of pine chips during digestion. It is assumed that for low proportions (up to 30 per cent) of pine in the blend, the yield and properties of the composite

pulp obtained from chip blends can be determined as the weighted average value of the component species from similar pulping conditions. The limitations of this assumption are considered later after a comparison of these estimates for pulp blends with the experimental data for pulping of chip blends. In this study the regression models developed earlier for the pulping of eucalypt and pine species are used to estimate the pulp yield and other properties at chemical charge and temperature conditions selected by a simple factorial design; these values are used to estimate the properties for the pulp blends.

5.3.2 Simulated Experimental Design and Models for Pulp Blends:

A simple factorial design (2^3) is used to estimate the effects of three important independent variables - pine fraction (0.1, 0.3), chemical charge (16, 18 per cent Na_2O) and temperature (165, 175°C) on the pulping behaviour of binary chip blends. The regression equations (5.3) and (5.4) are used to estimate the yield and properties of eucalypt and pine respectively and the results are used to predict the properties of the pulp from the binary chip blends, Table 5.41. The estimated values are correlated by linear regression equations for yield and Kappa number, equations (5.6) and (5.7), and the strength properties are correlated by second-order regression equation (5.8).

TABLE 5.41: ESTIMATES OF COMPONENT (EUCALYPT AND PINE) PULP AND PULP BLEND PROPERTIES*

Expt. no.	Pulping conditions			Pulp yield, %			Kappa no.		
	Pine fraction	Chemical charge,%	Temperature °C	E	P	EP	E	P	EP
1	0.1	16	165	49.62	47.87	49.43	31.81	76.23	36.24
2	0.3	16	165	49.62	47.87	49.08	31.81	76.23	45.12
3	0.1	18	165	47.52	43.26	47.08	24.98	61.06	28.61
4	0.3	18	165	47.52	43.26	46.23	24.98	61.06	35.83
5	0.1	16	175	48.18	46.51	48.08	23.52	51.71	26.32
6	0.3	16	175	48.18	46.51	47.69	23.52	51.71	31.96
7	0.1	18	175	45.10	42.90	44.88	21.33	38.40	23.01
8	0.3	18	175	45.10	42.90	44.44	21.33	38.40	26.43

* Estimated from regression equation for single species

E-Eucalypt P-Pine EP - Eucalypt-pine pulp blend

Table 5.41 contd

Expt. no.	Burst index (kPa. m^2g^{-1})			Tear index (mN m^2g^{-1})			Tensile index (N m g^{-1})		
	E	P	EP	E	P	EP	E	P	EP
1	5.15	6.09	5.25	8.23	12.54	8.66	70.06	86.86	71.14
2	5.15	6.09	5.43	8.23	12.54	9.52	70.06	86.86	73.30
3	5.98	6.47	6.02	7.35	12.47	7.87	76.05	86.65	77.11
4	5.98	6.47	6.12	7.35	12.47	8.79	76.05	86.65	79.23
5	5.46	5.82	5.50	7.43	10.95	7.78	75.57	84.52	76.47
6	5.46	5.82	5.57	7.43	10.95	8.49	75.57	84.52	78.26
7	5.47	6.50	5.58	8.28	11.51	8.60	72.17	82.37	73.19
8	5.47	6.50	5.79	8.28	11.51	9.25	72.17	82.37	75.23

E - Eucalypt P - Pine EP - Eucalypt-pine pulp blend

$$Y = 47.106 - 1.450\ x_1 - 0.846\ x_2 - 0.248\ x_8 \qquad (5.6)$$
$$(R^2 = 0.999,\ F = 256.3)$$

$$K = 31.690 - 3220\ x_1 - 4.76\ x_2 + 3.145\ x_8 \qquad (5.7)$$
$$(R^2 = 0.960,\ F = 62.3)$$

$$y = b_o + b_1x_1 + b_2x_2 + b_8x_8 + b_{12}x_1x_2 + b_{18}x_1x_8 + b_{28}x_2x_8 \qquad (5.8)$$

Values of the parameters in equation (5.8) for different pulp strength properties are given in Table 5.42.

5.3.3 <u>Three-Compartment Digester Experiments</u>:

Experiments were conducted in a 3-compartment digester for evaluating the simultaneous pulping characteristics of eucalypt, pine and eucalypt-pine chip blends, using the experimental design adopted above, Table 5.43A. The three compartments in the digester contained pine chips, eucalypt chips and chip blends (10-30 per cent pine). The weights (oven dry basis) of chips in the three compartments were: pine = 0.15 - 0.45 kg, eucalypt = 1.0 - 1.35 kg, and eucalypt-pine chip blend = 1.0 - 1.25 kg in the desired ratio; total weight of the chips was 2.5 kg. The weights of pine and eucalypt chips in the single species compartments also were in the same ratio as the chip blend.

The yield and Kappa number of eucalypt, pine and chip blends pulps were determined separately. The strength properties of the eucalypt and chip blend pulps were determine

TABLE 5.42: MATHEMATICAL MODELS FOR THE YIELD AND PROPERTIES OF PULP BLEND*

Parameter	Pulp yield	Kappa no.	Burst index	Tear index	Tensile index
b_o	47.106	31.69	5.657	8.624	75.49
b_1	-1.450	-3.220	0.220	0.011	0.699
b_2	-0.846	-4.76	-0.048	-0.094	0.296
b_8	-0.248	3.145	0.070	0.393	1.014
b_{12}	0	0	-0.145	0.383	-2.276
b_{18}	0	0	0.008	0.0	0.026
b_{28}	0	0	0.0	-0.053	-0.056
R^2	0.999	0.960	0.993	0.999	0.999
F-ratio	256.3	62.3	123.4	742.4	6119.4

*Estimates of pulp blend from component pulp properties, Table 5.41

$$y = b_o + b_1x_1 + b_2x_2 + b_8x_8 + b_{12}x_1x_2 + b_{18}x_1x_8 + b_{28}x_2x_8 \tag{5.8}$$

Coded variables:

x_1 = (chemical charge -17.0)/1.0

x_2 = (temperature - 170.0)/5.0

x_8 = (pine fraction - 0.2)/0.1

TABLE 5.43: KRAFT PULPING OF EUCALYPT-PINE CHIP BLENDS THREE-COMPARTMENT DIGESTER SYSTEM

(A) Range of Pulping Variables - Experimental Design

Variables	Symbol	Range/Levels -1	Range/Levels +1	Incremental change
Chemical charge, % Na_2O	x_1	16	18	+2
Temperature, °C	x_2	165	175	+10
Pine fraction	x_8	0.1	0.3	+0.2

Constants

Sulfidity, %	21	
Liquor:wood ratio,	3.6	
Time, min	60	
Chip size range, mm	-18+12	
Average chip thickness, mm		
Eucalypt:	3.5	(s.d. = 0.88)
Pine:	4.0	(s.d. = 1.5)
Time-to-temperature, min	90	

Coded Variables

x_1 = (chemical charge -17)/1.0

x_2 = (temperature -170)/5.0

x_8 = (pine fraction -0.2)/0.1

the quantity of pine pulps obtained was too small for refining in a Valley beater. The experimental results of these tests are given in Table 5.43B. The estimates obtained for the component pulps and the pulp blends (Table 5.41) are also included for comparison purposes. The experimental data are analyzed by Yates's algorithm (Table 5.44) to determine the effects of the three variables on different pulp properties. Second-order regression equations are derived to fit experimental data and the values of the parameters and the correlation coefficients are summarized in Table 5.45. The correlation was excellent for yield and all the properties of eucalypts (R^2 = 0.90 -0.99) and Kappa number of pine (R^2 = 0.997). The low correlation coefficient of the regression equation for screened yield of pine (R^2 = 0.82) may be attributed to the possible errors in yield determination caused by the small quantity of pine used (0.15 - 0.45 kg). Accountability of regression equations for the yield and properties of chip blend pulp was also very good (R^2 = 0.91 -0.99 except for tear index with R^2=0.80) and places good reliability on the models. The yield and properties of pulp from chip blend predicted using model equations (5.8, Table 5.45) are also given in Table 5.43.

5.3.4 Comparison of Eucalypt and Pine Data with Model Predictions (Single Species):

Experimental data obtained for eucalypt and pine pulps

TABLE 5.43: KRAFT PULPING OF EUCALYPT-PINE CHIP BLENDS
THREE-COMPARTMENT DIGESTER SYSTEM
(B) PULPING CONDITIONS AND EXPERIMENTAL RESULTS

Comparison of Experimental Data with Predicted (Regression models for chip blend) and Estimated (Regression Models for pulp blend) Values

Expt. no.		Pulping condition			Pulping Results			
		Pine fraction	Chemical charge, %	Temperature °C	AA consumption	Screened yield		
						E	P	EP
1	Expt.	0.1	16	165	13.1	48.20	55.2	47.90
	Pred.							47.65
	Est.					49.6	47.9	49.43
2	Expt.	0.3	16	165	12.3	47.8	46.3	47.20
	Pred.							47.43
	Est.					49.6	47.9	49.08
3	Expt.	0.1	18	165	13.7	47.6	42.6	45.40
	Pred.							45.63
	Est.					47.5	43.3	47.08
4	Expt.	0.3	18	165	13.8	48.4	46.9	45.90
	Pred.							45.66
	Est.					47.5	43.3	46.23
5	Expt.	0.1	16	175	13.6	45.9	49.0	43.00
	Pred.							43.23
	Est.					48.2	46.5	48.08
6	Expt.	0.3	16	175	13.7	45.8	44.6	43.30
	Pred.							43.06
	Est.					48.2	46.5	47.69
7	Expt.	0.1	18	175	14.8	44.6	47.8	43.60
	Pred.							43.36
	Est.					45.1	42.9	44.88
8	Expt.	0.3	18	175	14.7	45.0	44.7	43.2
	Pred.							43.43
	Est.					45.1	42.9	44.44

Expt. Experimental values
Pred. Regression of experimental data (chip blend)
Est. Estimates from single species (pulp blend, Table 5.41)

Table 5.43(B) contd

Expt. no.		Kappa no. E	Kappa no. P	Kappa no. EP	Burst index E	Burst index EP	Tear index E	Tear index EP	Tensile index E	Tensile index EP
1.	Exptl.	29.6	78.1	31.7	5.8	5.3	8.2	9.5	72.0	62.2
	Pred.			32.9		5.1		9.2		62.4
	Est.	31.8	76.2	36.2	5.1	5.2	8.2	8.6	70.0	71.1
2.	Expt.	26.8	71.1	36.8	4.3	5.1	7.7	8.4	65.8	69.5
	Pred.			35.5		5.2		8.7		69.3
	Est.	31.81	76.2	45.1	5.1	5.4	8.2	9.5	70.0	73.3
3.	Expt.	23.4	63.1	31.4	5.1	5.6	7.8	7.5	66.1	70.2
	Pred.			30.3		5.8		7.8		70.0
	Est.	25.0	61.1	28.6	6.0	6.0	7.4	7.9	76.1	77.[illegible]
4	Expt.	39.9	65.8	39.4	4.9	5.7	8.6	9.1	66.3	78.4
	Pred.			40.6		5.6		8.8		78.6
	Est.	25.0	61.1	35.8	6.0	6.1	7.4	8.8	76.1	79.2
5	Expt.	23.9	42.1	35.3	5.6	5.1	7.2	7.7	60.5	72.7
	Pred.			34.1		5.2		8.0		72.5
	Est.	23.5	51.7	26.3	5.5	5.5	7.4	7.8	75.6	76.5
6	Expt.	21.8	41.2	27.2	4.7	5.3	7.1	8.4	55.2	76.5
	Pred.			28.4		5.2		8.0		76.7
	Est.	23.5	51.7	32.0	5.5	5.6	7.4	8.5	75.6	78.3
7	Expt.	21.4	33.1	22.1	4.5	4.7	6.2	7.6	55.5	57.1
	Pred.			23.3		4.6		7.3		57.3
	Est.	21.3	38.4	23.9	5.5	5.6	8.3	8.6	72.2	73.2
8	Expt.	24.8	35.5	26.7	4.1	4.1	7.5	8.6	68.0	54.4
	Pred.			25.5		4.2		8.9		54.2
	Est.	21.3	38.4	26.4	5.5	5.8	8.3	9.3	72.2	75.2

Expt. Experimental values

Pred. Regression of experimental data (chip blend)

Est. Estimates from single species (pulp blend, Table 5.41)

TABLE 5.44: KRAFT PULPING OF EUCALYPT-PINE CHIP BLENDS

THREE-COMPARTMENT DIGESTER SYSTEM

SUMMARY OF DATA ANALYSIS BY YATES'S ALGORITHM

CHIP BLEND PULP

Effect and Interaction		Screened pulp yield %	AA consumption %	Kappa no.	Burst index	Tear index	Tensile index
Average effect		44.94	13.71	31.33	5.12	8.36	66.50
Pine fraction (f)		-0.08	-0.18	2.40[a]	-0.14	0.53[a]	1.92[a]
Chemical charge (AA)		-0.83[a]	1.07[a]	-2.85[a]	-0.18	-0.31	-2.98[a]
Temperature, (T)		-3.33[a]	0.98[a]	-7.00[a]	-0.65[a]	-0.61[a]	-7.18[a]
Interactions	(f x AA)	0.13	0.18	3.90[a]	-0.16	0.72[a]	0.85
	(f x T)	0.03	0.18	-4.15[a]	-0.07	0.30	-5.80[a]
	(AA x T)	1.08[a]	0.02	-4.00[a]	-0.64[a]	0.38	-11.35[a]
	(f x AA x T)	-0.48	-0.27	2.45[a]	-0.31	-0.64	0.40

a - significant at 95 per cent confidence level.

TABLE 5.45: KRAFT PULPING OF EUCALYPT-PINE CHIP BLENDS
THREE-COMPARTMENT DIGESTER SYSTEM
MATHEMATICAL MODELS

(A) EUCALYPT AND PINE (SINGLE SPECIES)

Para-meters	Eucalypt					Pine	
	Screen-ed yield	Kappa no.	Burst index	Tear index	Tensile index	Screened yield	Kappa no.
b_o	46.663	26.450	4.900	7.527	63.709	47.138	53.750
b_1	-0.263	0.925	-0.208	-0.023	0.301	-1.638	-4.375
b_2	-1.338	-3.475	-0.153	-0.550	-3.881	-0.613	-15.775
b_8	0.088	1.875	-0.390	0.190	0.133	-1.513	-0.350
b_{12}	-0.263	-0.800	-0.170	-0.130	1.691	1.363	0.700
b_{18}	0.213	3.100	0.218	0.330	3.011	1.813	1.625
b_{28}	-0.013	-1.550	0.033	0.113	1.644	-0.363	0.725
R^2	0.996	0.907	0.961	0.999	0.936	0.828	0.997
F-ratio	43.1	1.62	4.1	509.4	2.4	0.799	70.7

$$y = b_o + b_1x_1 + b_2x_2 + b_8x_8 + b_{12}\,x_1x_2 + b_{18}\,x_1x_8 + b_{28}\,x_2x_8 \qquad (5.8)$$

Coded variables:

x_1 = (chemical charge -17.0)/1.0

x_2 = (temperature-170.0)/5.0

x_8 = (pine fraction -0.2)/0.1

Table 5.45 Contd

(B) CHIP BLEND

Parameters	Screened yield	AA consumption	Kappa no.	Burst index	Tear index	Tensile index
b_o	45.56	13.71	31.33	5.122	8.35	66.49
b_1	-0.687	0.537	-1.425	-0.090	-0.148	-1.488
b_2	-1.737	0.487	-3.500	-0.325	-0.308	-3.588
b_8	0.013	-0.088	1.200	-0.070	0.258	0.961
b_{12}	0.613	0.013	-2.000	-0.322	0.196	-5.676
b_{18}	0.063	0.088	1.950	-0.078	0.369	0.423
b_{28}	0.188	0.088	-2.075	-0.033	0.144	-2.911
R^2	0.995	0.966	0.948	0.905	0.796	0.999
F-ratio	34.43	4.84	3.09	1.59	10.65	234.12

$$y = b_o + b_1x_1 + b_2x_2 + b_8x_8 + b_{12}\, x_1x_2 + b_{18}\, x_1x_8 + b_{28}\, x_2x_8 \quad (5.8)$$

Coded variables:

x_1 = (chemical charge -17.0)/1.0

x_2 = (temperature -170.0)/5.0

x_8 = (pine fraction -0.2)/0.1

from the 3-compartment digester are compared with the predictions based on the single species models in Table 7.43B.

The yield of eucalypt pulp is lower and the yield of pine pulp is higher than the estimated values. Consequently, the Kappa number of eucalypt pulp is also lower and that of pine pulp higher than the predicted values based on the model equations for single species. This is caused by the relatively faster delignification rates of eucalypts and the reduction in alkali available for delignification of pine chips. This also can be attributed to the slightly lower chemical charge and temperature levels adopted compared to pulping pine alone. These observations are in agreement with the results reported by Hunt and Hatton (1978).

The screening reject of eucalypt was small (0.1-0.3 per cent) while pine pulps had higher rejects (1.3 - 3.8 per cent at 165°C, 0.6 - 1.6 per cent at 175°C). The screen rejects from the pulps of chip blends was low (0.2 - 0.8 per cent) since pine constituted only upto 30 per cent of the blend.

The burst and tensile indices for eucalypt pulp were observed to be lower and the tear index was either comparable or slightly higher than the estimated values. This may be attributed to the lower yield caused by the removal of more lignin and hemicelluloses during pulping. The results are in agreement with similar observations reported by Hunt and Hatton (1978).

5.3.5 Analysis of Chip Blend Pulping Data:

The experimental data for chip blend pulps are analyzed by Yates's algorithm and summarized in Table 5.44. The major observations are given below:

1. Temperature has the most significant influence on yield while pine chip fraction has essentially no effect. Chemical charge and its interaction with temperature show an intermediate effect.
2. The active alkali consumption is independent of pine fraction and increases with chemical charge and temperature.
3. Kappa number of the pulp from the chip blend increases with the pine content and is strongly dependent upon chemical charge and temperature.
4. Burst index decreases with temperature and is not influenced by chemical charge or pine fraction.
5. Tear index and tensile index improve with pine content. Temperature has a strong influence on tensile index and an increase in temperature decreases it. Chemical charge interacts strongly with temperature and the tensile index of the pulp decreases considerably when both these variables are at the higher level.

The net effects of pine chips addition (upto 30 per cent) to eucalypt include: constant pulp yield, higher Kappa number, improved tear and tensile indices, and constant burst index.

5.3.6 Comparison of Model Predictions (Chip Blend Pulp vs Pulp Blend):

The estimated properties of the pulp blend (Table 5.41) are compared with the **predictions** based on the models (Table 5.45) for pulping chip blends in Table 5.43B and the following observations are obtained:

1. The estimated yields agree within $\pm$ 1 per cent of the predicted values.
2. The agreement of observed Kappa number with the estimates is poor owing to the possible heterogeneous character of the residual lignin in the component pulps.
3. Burst index showed good agreement at 165°C while the observed values are lower than the estimates at 175°C.
4. Tear index estimates showed good agreement with the model predictions.
5. The chip blend model predicts lower tensile index and the deviation increased with pulping temperature.

The above observations tend to support the linear blending rule based on the component properties for the estimation of yield and tear index of the pulp from chip blends. The rule can also be applied to predict burst index and tensile index for pulping at 165°C. The results have shown that within the experimental region studied eucalypt-pine chip blend (70:30) pulped at 165°C with 18 per cent active alkali would give the maximum strength properties with 45.9 per cent screened yield at a Kappa number of 40 with burst index = 5.72, tear index = 9.11 and tensile index = 78.4.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS

6.1 Summary:

This work was carried out for investigating the pulping characteristics of plantation grown eucalypt (*E. tereticornis* hybrid), abnormal twisted chir pine (*P. roxburgii*) and eucalypt-pine chip blends. Proximate chemical composition and pulp fiber dimensions of the two species were determined to characterize the raw materials. Pulping characteristics of eucalypt, pine and chip blends were studied in three separate sets of experiments through sequential experimental designs. Manually screened and handsorted mill chips were used for pulping in a rotary Weverk digester.

Seven major kraft pulping variables were recognized - chemical charge, temperature, sulfidity, time-to-temperature, time-at-temperature, liquor-to-wood ratio and chip thickness. The dependent variables investigated include - yield, Kappa number, black liquor solids, active alkali consumption, and pulp strength properties - tear, burst, tensile and folds.

Simple factorial designs were used to determine the effects of time-to-temperature and chip size. The interacting influence of time-to-temperature(heating period) and pulping temperature determined the uniformity of both eucalypt and

pine pulps. A constant heating period of 90 min was selected for all the experiments. It was observed that chip size (thickness range 2-6 mm) was not a significant variable for the pulping of eucalypts while a lower pine **chip** size range improved the yield of screened pulp. Manually screened eucalypt chips (fraction - 25+16 mm with average chip thickness - 4.4mm) and pine chips (fraction - 18+12 mm with average chip thickness - 4.0 mm) were used for the pulping experiments. Thus the number of variables was reduced to five for developing mathematical models for the kraft pulping of eucalypt and pine chips.

The influence of the remaining five variables were studied using a sequential design approach for eucalypts based on (1) a half-fraction factorial design, and (2) second-order central composite rotatable design. The data from the fractional factorial design were analyzed using Yates's algorithm. Second-order regression equation models were obtained to fit the experimental data from the above experiments using a digital computer (DEC system - 1090). Regression analysis gave good correlation of yield and Kappa number data while the correlation was fair for the strength properties. The models were further used to locate the optimum pulping conditions for maximum tearing strength using Constrained Rosenbrock Method. Data from pulping experiments conducted at

these estimated optimum conditions agreed well with the predicted properties and showed good reliability of the models.

Experimental work for pine chips was similar to the factorial designs used for eucalypts and the data correlated by second-order regression equations. The correlation coefficients for yield and Kappa number were good and satisfactory for strength properties. The range of conditions used for pulping pine was rather narrow to locate the optimum conditions; however the best conditions to pulp pine chips to give maximum tearing resistance were obtained and confirmed experimentally.

The models for eucalypt and pine pulping have been graphically represented to illustrate the effects of the different variables about the central point conditions as well as by two-dimensional contour plots for the response with chemical charge and temperature.

A comparison of the strength properties of eucalypt and pine pulps showed that the latter had superior tear, burst and folding endurance and comparable tensile strength. The strength properties of eucalypt pulp can be improved by blending with pine pulp or by using a chip blend for pulping.

Experiments conducted in a 3-compartment digester with chip blends containing 10-30 per cent pine showed that the effects of pine chip addition to eucalypt are: constant

total pulp yield, higher Kappa number, improved tear and tensile indices, and constant burst index. Regression equations were developed for the pulping of eucalypt-pine chip blends. It was also shown that the linear blending rule based on the component pulp properties can be used for the estimation of total yield and tear index of the pulp blends and agreed with the predictions based on chip blend models.

6.2 Recommended Future Studies:

In this study statistical experimental designs have been successfully used to develop mathematical models for the **kraft** pulping of eucalypt, pine and binary chip blends. Eucalypt pulping experiments cover an adequate range of pulping variables relevant for pilot plant/commercial applications. The range selected for pine and chip blend experiments have a bias towards the range adopted for eucalypt, constituting over 70 per cent of the digester furnish.

The range of pulping variables used for pine have only given the best pulping conditions and a wider range is recommended for the location of the true or global optimum.

The heterogeneous and abnormal character of the pine chips have contributed to somewhat higher standard deviations in Kappa number and strength properties of pine pulp.

The correlation coefficients for strength properties of both eucalypt and pine chips are satisfactory with R^2=0.7-0.8;

the correlation coefficient for tear index of pine was poor ($R^2 = 0.5$). The low correlation coefficients for the strength properties indicate the possible influence of additional parameters besides the five digester variables considered. These can be the influence of the inevitable variations associated with the post-digestion steps - beater operation, handsheet preparation and conditioning, sensitivity and precision of the testing equipment. These variations could be minimized by using pulp refining and test equipment of better precision and improve the correlation of the data obtained from a mill control laboratory equipment.

Further studies are also recommended to study the optimum proportions of binary chip/pulp blends to get composite pulp of the desired strength properties incorporating the superior qualities of both the eucalypt and pine. A detailed study is recommended over a wider range of the pulping variables. Correlation of the strength property data should also include the degree of pulp refining as an additional parameter for binary chip/pulp blends.

REFERENCES

Algar, W.H., "The Utilization of Short-Fibered Pulps in Paper making", Proceedings of the Conference on Pulp and Paper Development in Asia and the Far East, Vol. II, p.471.(1960).

Almin, K.E. and Alf de Ruvo, "Polynomial Representation of Pulp Mixture Properties," Svensk Papperstidning 70(24): 846-850 (1967).

Arlov, A.P., "Beating and Blending of Bleached Softwood and Hardwood Pulps", Svensk Papperstidning 66(9): 333-42 (1963).

Bailey, R.N., P. Maldonado, S.W. McKibbins, and Mae-G.Traver, "A Statistical Analysis and Optimization Procedure for the Kraft Pulping Process", Tappi, 52(7), 1272-1275 (1969).

Beveridge, G.S. and R.S. Schechter, "Optimization: Theory and Practice", McGraw Hill, Tokyo (1970).

Bhat, R.V. and M.M. Singh, "Indigenous Cellulosic Raw Materials for the Production of Pulp, Paper and Board. Part XXVII - Wrapping Papers from Chir (Pinus longifolia Roxb.) of Twisted Grain", Indian Forester 81(12): 765-772 (Dec. 1955).

Bhaumick, S.K. and K.L. Ghosh, "The Pulping Characteristics of Pinus Khasya", Ippta, 12(1), 31 (1975).

Bolch, B.W., and C.J. Huang, "Multivariable Statistical Methods for Business and Economics", Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1974).

Borlew, P.B. and R.L. Miller, "Chip Thickness: A Critical Dimension in Kraft Pulping", Tappi, 53(11); 2107 (1970).

Bovin, A. and A.Teder, "Some Aspects on Additivity," International Symposium on Paper Pulp Characterization, Ronneby, May 24-26, 1971, STFI, Sweden.

Box, M.J., "A New Method of Constrained Optimization and a Comparison with other Methods", Computer J., 8: 42-52 (1965).

Box, G.E.P., W.G. Hunter and J.S. Hunter, "Statistics of Experimenters: An Introduction to Design, Data Analysis, and Model Building," John Wiley & Sons, Inc., (1978).

Brecht, W., "The Mixing of Different Half-Stuffs and Influence on the Physical Properties of Papers", (in German), Svensk Papperstidning 66(5): 159-67 (1963). CA 58:14292e (1963).

Carrol, C.W., "Development of a Rate Expression for Kraft Pulping Reactions", Tappi 43(6), 573-79 (1960).

Chari, N.C. , "Integrated Control System Approach for Batch Digester Control", Tappi 56(7): 65-68 (1973).

Chen, R., J.J. Garceau, and B.V. Kokta, "Hardwood Mixed with Softwood in Kraft Pulping: Optimization of Utilization", Tappi, 61(7), 35 (1978).

Clark, James d'A., "Pulp Technology and Treatment for Paper," Miller Freeman Publications, Inc., San Fransisco, 1978.

Colley, J., "Properties of Blends of E. tetrodonta and P. radiata Pulps", Appita, 27(1): 35-41 (1973).

Colombo, P., D. Corbetta, A. Pirotta and G. Ruffini, "The Influence of Thickness of Chips on Pulps Properties in Kraft Cooking", Svensk Papperstidning, 67(12), 505 (1964).

Davies, O.L., Editor, "The Design and Analysis of Industrial Experiments," Oliver and Boyd, London, 1967.

De Oliviera, R.C., C.E.B. Foelkel and J.L. Gomide, "Wood Mixtures of Pinus Strobus var. Chiapensis and Eucalyptus urophylla in Kraft Pulping", Papel 1981, (42), 67-78 (Portuguese). Chemical Abstract, 95: 44993s(1981)

De Oliveira, R.C., Foelkel, C.E.B. and J.L. Gomide, "Physico-mechanical Properties of Kraft Pulps Produced by Cooking Mixtures of Pinus strobus var Chiapensis and Eucalyptus urophylla of hybrid Origin", Rev. Arvore 1980, 4(2), 188-202 (Spanish). C.A. 95:82636k (1981).

Edwards, Louis and S.E. Norberg, "Alkaline Delignification Kinetics: A General Model Applied to Oxygen Bleaching and Kraft Pulping", Tappi 56(11): 108-111 (1973).

Edwards, L., S.E. Norberg and A. Teder, "Kinetics of the Delignification in Kraft Pulping. II. Bulk Delignification of Birch", Svensk Papperstidning 77(3): 95-98 (1974).

Enkvist, T., Holm, B., Kourula, A., and J.E. Martelin, "The Role of Oxidation Reduction Potential and Hemicellulose During Sulfate Digestion", Paperi Ja Puu, 39: 297-302 (1957). CA 51: 18581f (1957).

Franklin, E.C., "Yield and Properties of Pulp from Eucalypt Wood Grown in Florida", Tappi, 60(6), 65 (1977).

Foelkel,C.E.B. and C. Zvinakevicius, "Hardwood Pulping in Brazil", Tappi 63(3):39-42 (1980).

Garceau, J.J., K.N. Goel, and A.M.Ayroud, "Optimization of High-Yield Kraft Pulping Variables to Obtain Maximum Ring Crush", Tappi, 57(6), 137 (1974).

Garceau, J.J., K.N. Goel, and A.M.Ayroud, "Optimization of High-Yield Kraft Pulping Variables: Effect of H-factor.", Tappi, 57(8), 127 (1974a).

Gierer, J., Lenz, B., and N.H. Wallin, "Reactions of Lignin During Sulfate Cooking. V. Model Experiments on the Splitting of aryl-alkyl ethers Linkages by 2N NaOH and by White Liquor", Acta Chem. Scand., 18(6):1469-76 (1964). C.A.62: 2910d (1965).

Goel, K. and A.M.Ayroud, "Hardwood and Softwood Ternary Pulp Blends for Specific End Uses", Consolidated-Bathurst Ltd. Research and Development Centre, Grand'Mere, Quebec, Canada (Personal communication, 1980).

Guha, S.R.D., M.M.Singh,G.M. Mathur, Y.K. Sharma, K. Kumar and R.C. Thapliyal," Utilization of Eucalyptus hybrid (Mysore gum) Grown in U.P. for the Production of Wrapping Paper, Writing Paper and Rayon Grade Pulp", Proceeding of the Symposium on Utilization of Hardwoods for Pulp and Paper (1968): page 103-112, F.R.I.& C., Dehradun, India.

Guha, S.R.D., Indian Forester, 95(8): 579 (1969).

Guha, S.R.D., Y.K. Sharma, R. Pant, S.P.Singh, D.K. Jain and B.G. Karia, "Pulping Qualities of Eucalyptus Hybrid Grown in U.P.", Indian Forester, 99(6): 349-51 (1973).

Guha, S.R.D. and M.M. Singh,"Results of Laboratory Trials with E. hybrid wood, Fresh and After Storage for News Print", Indian Forester, 101(8): 476-83 (1975).

Hannah, B.C.,Fergus, B.J. and R.N. Jones, "Kraft Pulping and Bleaching Studies on Young Exotic Hardwood Species", Appita 30(6): 483-7 (1977).

Hartler, N. and W. Onisko, "The Interdependence of Chip Thickness, Cooking Temperature and Screenings in Kraft Cooking of Pine", Svensk Papperstidning, 65(22): 905-910 (1962).

Hannah, B.C.and D.A.Swann, "Kraft Co-cooking of Hardwoods and Softwoods", Appita 34(5): 383-86 (1981).

Hatton, J.V., J.L. Keays and J.Hejjas, "Effects of Time, Temperature, and Effective Alkali in Kraft Pulping of Western Hemlock", Pulp & Paper Mag. Can. 73(4): T103-T109 (1972).

Hatton, J.V. and J. Hejjas, "Effects of Time, Temperature, and Effective Alkali in Kraft Pulping of Trembling Aspen (Populus Tremuloides Michx.)", Pulp & Paper Mag.Can. 73(9): T218-222 (1972).

Hatton, J.V., "Development of Yield Prediction Equation in Kraft Pulping", Tappi 56(7): 97-100 (1973).

Hatton, J.V. and J.L. Keays, "Effect of Chip Geometry and Moisture on Yield and Quality of Kraft Pulps from Western Hemlock and Black Spruce", Pulp Paper Canada 74(1): T11 (1973).

Hatton, J.V., "The Potential of Process Control in Kraft Pulping of Hardwoods Relative to Softwoods",Tappi 59(8): 48-51 (1976).

Hatton, J.V., "Kraft Pulping Equations: Comparison of Linear with Non-linear Forms", Tappi 59(12): 132-133 (1976).

Hatton, J.V., "Thin Chips Give Highest Screened Yields in Mixed Softwood/Hardwood Kraft Pulping", Tappi 60(5): 116-117 (1977).

Hatton, J.V., "Is Tappi Ready for a New Chip-Quality Standard Method?" 1978 Tappi Pulping Conference, pp 115-120 (1978).

Hemmerle, W.J., "Statistical Computation on Digital Computer," Blaisdell Publishing Co., Waltham, Massachusetts, (1967).

Higgins, H.G., "The Long and Short of Papermaking", The Australian Timber Journal, 35(1), 26 (1969).

Higgins, H.G., "Technical Assessment of Eucalypt Pulps in the Papermaking Economy", Appita, 23(6) : 417-426 (1970).

Hillis, W.E. Editor, "Wood Extractives and their Significance to e Pulp and Paper Industries", Academic Press, New York and London (1962).

Himmelblau, D.M., "Process Analysis by Statistical Methods", John Wiley & Sons Inc., New York (1968).

Hinrichs, D.D., "The Effect of Kraft Pulping Variables on Delignification", Tappi, 50(4), 173-175 (1967).

Hunt, K. and J.V. Hatton, "Increased Pulp Production by Use of Hardwoods in Softwood Kraft Mills", Pulp Paper Canada 77(12): T271-5 (1976).

Kerr, A.J., "The Kinetics of Kraft Pulping - Progress in the Development of a Mathematical Model," Appita 24(3), 1-9 (1970).

Kerr, A.J., "The Kinetics of Kraft Pulping - batch Digester Control", Tappi 59(5): 89-91 (1976).

Kleinert, T.N., "Mechanisms of Alkaline Delignification - I. The Overall Reaction Pattern", Tappi 49(2):53-7 (1966).

Kleppe, P.J., Kraft Pulping, Tappi 53(1): 35 (1970).

Kuester, J.L. and J.H. Mize, "Optimization Techniques with Fortran", McGraw Hill, New York (1973).

Kulkarni, G.R. and W.J. Nolan, "The Mechanism of Alkaline Pulping", Paper Ind. 37(2): 142 (1955).

Lapointe, A., "How to judge Chip Suitability", Pulp & Paper Canada, 80(11): T382-86 (1979).

Larocque, G.L. and O. Maass, "The Mechanism of Alkaline Delignification of Wood", Can. Journal of Research 19B(1): 1-16 (1941).

Lemon, S. and Ants Teder,"Kinetics of the Delignification in Kraft Pulping. I. Bulk Delignification of Pine", Svensk Papperstidning 76(11): 407-14 (1973).

Lin,C.P., W.Y. Mao and C.Y. Jane, "Development of Kappa number Prediction Equation in Kraft Pulping of Hardwoods", Tappi 61(2): 72 (1978).

Lodzinski, F.P. and T.Karlsson, "The ASEA-MoDO Kappa Batch System: Theory, Application Considerations and Models", Tappi, 59(9): 88-91 (1976).

Luzina, L.I., "The Dependence of Kraft Pulp Yield on Cooking Conditions",(Russian), Bumazhn. Prom. 8:7 (1966). C.A. 65:15653e (1966).

Macdonald, R.G., Editor, "Pulp and Paper Manufacture Vol.I The Pulping of Wood, McGraw Hill Book Co., New York, 1969.

Mathur, V.K., "Response Surface Analysis for Optimization of Yield in Polysulfide - Kraft Pulping", Tappi Pulping Conference, 47-65 (1978).

McKibbins,S.W., P. Maldonado, R.N. Bailey, and J. Sackellares, "Statistical Analysis of Kraft Pulp Mill Digester Operation", Tappi, 53(9), 1750 (1970).

Nordeman, D.R., "Optimization of Hardwood Pulp Usage by Calculation of Properties of Pulp Blends",Tappi, 56(5): 100-103 (1973).

Oye, Raysabro, Tadao Mizuno and Nobuhiro Hato, "The Influences of the Extractives in Eucalyptus Woods on the Viscosity of Concentrated Black Liquor", Japan Tappi 26(12): 20-29 (1972).

Oye, R., N. Hato, and T. Mizuno, "The Extractives in Eucalyptus Woods and Their Influences on the Properties of Black Liquor at Evaporation and Combustion", Japan Tappi 27(2): 24-32 (1973).

Peckham, J.R. and May, M.N., "Refining of Softwood and Hardwood Kraft Pulps Separately and as Mixtures", Tappi 42(7): 556-8 (1959).

Phillips, F.H., R.B. Bain, and A.J. Watson, "An Assessment of the Pulping Potential of Various Western Australian Wood Species", Paper No.49, CSIROA, Melbourne, Australia (1967).

Rosenbrock, H.H., "An Automatic Method for the Greatest or Least Value of a Function", Computer J., 3:175-184 (1960).

Rydholm, S.A., "Pulping Processes", Interscience Publishers, New York (1965).

Smith, R.W., "Some Aspects of the Kraft Pulping of Eucalyptus at Maryvale Mill", Appita Proceedings, p.60 (1956).

Srivastava, J.S. and G.M. Mathur, "Chemical Pulps for Writing and Printing Papers from Eucalyptus Grandis", Indian Pulp Paper 19(3): 215-16 (1964).

Steffes, F.J., "Commercial Screening for Overthick Chip Removal", 1978 Tappi Pulping Conferences, pp:107-113 (1978).

Unkalkar, V.G., Tripathi, R.S. and M.B. Jauhri, "Paper making Potential of Blends of Bamboo and Eucalyptus Sulfate Pulps", Ippta 11(1): 20-26 (1974).

Wallin, Gunnar and Sture Noreus, "Computer Control of Batch Digesters", Svensk Papperstidning 76(9): 329-334 (1973).

Watson, A.J., and W.E.Cohen, "Pulping of Eucalyptus - A Historical Survey", Appita, 22(4), 17 (1969).

Wells, C.H., E.C.Johns and F.L. Chapman, "Computer Control of Batch Digester Using a Kappa number Model", Tappi 58(8): 177-181 (1975).

Wilder, H.D. and E.J. Daleski, Jr., "Kraft Pulping Kinetics: I. Literature Review and Research Program", Tappi 47(5) 270-275 (1964).

Wilder, H.D. and E.J. Daleski, Jr., "Delignification Rate Studies, Part II of a Series on Kraft Pulping Kinetics", Tappi 48(5):293-97 (1965).

APPENDICES

APPENDIX I

REGRESSION ANALYSIS BY THE METHOD OF LEAST SQUARES

The first order approximation of the response surface gives equation (A.1) consisting of only the linear terms of the variables,

$$y = b_o + \sum_{i=1}^{k} b_i x_i \tag{A.1}$$

The coefficients b_o and b_i are estimated by the method of least squares, represented in the matrix notation by equation (A.2),

$$\underline{b} = (\underline{X}^T \underline{X})^{-1} \underline{X}^T \underline{Y} \tag{A.2}$$

$$b_o = \bar{y} - \sum_{j=1}^{k} b_j \bar{x}_j \tag{A.3}$$

where $\underline{X}$ - design matrix

$\underline{Y}$ - vector of observed responses

$\bar{x}_j$, $\bar{y}$ - mean values

$$\bar{y} - \sum_{i=1}^{N} y_i/N \tag{A.4}$$

The multiple correlation coefficient (R^2) is determined from equations (A.5) to (A.7).

$$R^2 = \frac{\text{Sum of squares due to regression (SSR)}}{\text{Sum of squares corrected total (SST)}} \tag{A.5}$$

where,

$$SST = S + SSR$$

$$\sum_{i=1}^{N} (y_i - \bar{y})^2 = \sum_{i=1}^{N} (y_i - y_i')^2 + \sum_{i=1}^{N} (y_i' - \bar{y})^2 \tag{A.6}$$

$$SSR = \underline{b}^T (\underline{x}^T \underline{y}) = \sum_{i=1}^{N} (y_i' - \bar{y})^2$$

$$SST = \underline{y}^T \underline{y} = \sum_{i=j}^{N} (y_i - \bar{y})^2 \tag{A.7}$$

A linear model adequately fits the data when $R^2 = 0.95 - 1.0$. The correlation coefficient can be improved by including additional terms in the response function. A second order polynomial with linear, second order and interaction terms, equation(A.8) is considered next to represent the data.

$$y = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i<j}^{k} b_{ij} x_i x_j \tag{A.8}$$

Experimental data from a simple 2-level factorial design suffice only for a polynomial having linear and interaction terms. Estimation of the parameters of second order terms (in the regression equation) require 3-level factorial designs or central composite rotatable designs.

Adequacy of the Model:

The adequacy of the models can also be tested by calculating the Fisher ratio (F. test), equation (A.9).

$$F_{calc.} = \frac{s_{ad}^2}{s_Y^2} \tag{A.9}$$

where s_{ad}^2 - variance of the model

s_Y^2 - experimental error variance

$$s_{ad}^2 = \sum_{i=1}^{N} (y_i - y_i')^2 / (N-(k+1))$$

$$= \frac{\text{Residual sum of squares (least square)}}{\text{Number of degrees of freedom}}$$

where, the number of degrees of freedom is equal to the difference between the number of observations and the numbers of parameters estimated.

$$s_Y^2 = \sum_{i=1}^{n} (y_i - \bar{y})^2 / (n-1)$$

where $\bar{y}$ - mean value of response for the repeated observations

n - number of replicated experiments.

The model is taken to be adequate if,

$$F_{calc} < F_{0.05} \quad (N-(k+1),\ n-1)$$

where $F_{0.05}$ (N-(k+1),n-1) is the tabulated value (Himmelblau, 1968) of F at a confidence level of 95 per cent with N-(k+1) degrees of freedom in the numerator and (n-1) degrees of freedom in the denominator.

Significance of Parameters:

A general first order polynomial with five variables will have six parameters, whereas the second order polynomial expression will have 21 parameters. These polynomials can be simplified by retaining only the statistically significant parameters and deleting the remainder which have a minor contribution to the response. Statistical significance of the parameters is estimated by the associated error variance compared to the experimental error variance.

The significance of the coefficients is evaluated by the following method (Hemmerle, 1967) using students' 't' test.

The variance-covariance matrix of the regression coefficients is first evaluated by using the formula given by equation (A.10).

$$\underline{S}^2(b) = \frac{\underline{Y}^T \underline{Y} - \underline{b}^T \underline{X}^T \underline{Y}}{(N-p)} \quad (\underline{X}^T \underline{X})^{-1} \qquad (A.10)$$

where $\underline{X}$ - matrix of independent variables (design matrix)

$\underline{Y}$ - vector of observed responses

$\underline{b}$ - vector of estimated coefficients or parameters (slopes)

N - total number of experiments in the design

p - number of coefficients (parameters)

The students' 't' value for a particular coefficient b_j is calculated using the equation (A.11).

$$t_{calc} = \frac{b_j}{s(b_j)} \tag{A.11}$$

where t_{calc} = calculated students' 't' value

$s(b_j)$ = variance of the jth coefficient b_j obtained from variance-covariance matrix, $\underline{S}(b)$. (It is also equal to the standard error of estimate of the slope).

The value for degrees of freedom used in the equations and the statistical tables will depend upon the number of coefficients in the proposed response function. If the absolute value of t_{calc} is found less than the tabulated value ($t_{0.95}$, N-p), the coefficient is considered insignifica all such coefficients can be eliminated in the subsequent iteration. This procedure is continued to obtain an expressio having only the significant coefficients.

The computer program used for regression analysis (Bolch and Huang, 1974) based on equation(A.8) by least squares method also gave values of b_o (intercept), coefficient or slopes (b_i, b_{ii}, b_{ij}), standard error of estimate of each coefficients $s(b_j)$, mean standard deviation, multiple correlat coefficient (R^2) and F-ratio. Thus, the value of 't' can be calculated simply by dividing the coefficient with its standa error of estimate. The tabulated value of 't' at 95 per cent confidence level is compared with the calculated value of 't' to determine the significance of the coefficients.(A computer program for the Regression Analysis is given in Appendix VIII)

APPENDIX II

CHEMICAL COMPOSITION AND FIBER DIMENSIONS OF EUCALYPT AND PINE

EUCALYPT (Eucalyptus tereticornis):

Chemical Composition: Eucalypt wood contains an appreciable concentration of polyphenolic compounds as extraneous components. These include some free ellagic acid and gallic acid and monomeric as well as condensed polymeric fragments based on compounds like leucoanthocyanins, catechins, stilbenes, ellagitannins etc. and their derivatives (Hillis, 1962). The precise chemical identity of the polyphenolic extractives of the various eucalypt species is not known and are strongly dependent upon age and species. Presence of such compounds interferes with the determination of Klason lignin during proximate analysis of wood meal. These extractives are not removed by the solvents commonly used in preparing extractive-free wood meal. However, an alkali extraction step removes most of these polyphenolic compounds. Extractive-free eucalypt wood meal is prepared by a sequential extraction treatment using alkali (1.0 per cent NaOH), and boiling water.

The results of the proximate analysis are shown in Table 5.1 for the (-40 +60 mesh) wood meal of samples A and B. Analysis of the (-60 mesh) fraction are also given for sample B. The number of determinations was 2-3 for all and 4-5 for extracti free lignin and holocellulose. The age of the trees from

which these logs came varied in the range 8–10 years. The values in Table 5.1 lead to the following observations:

1. Extractives constitute upto one sixth of the wood meal.
2. Klason lignin content of the original wood meal is about 10 per cent higher compared to the extractive-free material and is caused by the condensation of the polyphenolic extractives with lignin during carbohydrate hydrolysis.
3. Even though the fine fraction (–60 mesh) of the wood meal contains upto 5 per cent more lignin, the extractive free substance contains 5 per cent less lignin than the corresponding –36 +60 mesh fraction. This is caused by the relatively higher proportion (about 6 per cent) of polyphenolic compounds in the fines fraction as shown by the solubility in 0.5 per cent NaOH.
4. Extractive-free wood meal contains about 30 per cent lignin (s.d. = 0.710), 50 per cent α-cellulose, and 17 per cent pentosans, comparable to the values reported by Guha (1969). Similar chemical composition is reported for Brazilian plantation grown eucalypts (Foelkel and Zvinakevicius, 1980).

Basic Density: Average density of eucalypt tereticornis chips (air dry) was determined by the usual water displacement method to be 0.66 g cm^{-3}. Basic wood density is defined as oven-dry weight per volume of green wood and the shrinkage of wood on drying is around 10-15 per cent. Basic density is quite closely related to lumen/diameter ratio. Hardwood fibers with a smaller diameter will also have a smaller value of wall thickness than the softwood. Basic wood density can vary from 0.3-0.7 for most of hardwoods and softwood. Because of shrinkage, the value will be higher if determined on air dry chips. (Mac Donald, 1969), however, even larger values are also reported. Algar (1960) has reported values of wood density (in the range of 0.41 - 0.86) for various eucalypt species. Mature/overmature eucalypts have a higher density. Franklin (1977) has reported a density of 0.512 g cm^{-3} for E. tereticornis grown in Florida (U.S.A.). The most common plantation grown eucalypt species used for pulping have basic density in the range 0.4 - 0.6 g cm^{-3} (Foelkel, 1980).

Fiber Dimensions: Two unbeaten pulp samples obtained from the pulping experiments at central point conditions were chosen for fiber dimension measurement (Cook nos. E-49, E-50). The results correspond to number average of 260 measurements (20 slides containing 12-15 fibers each). These values are length - 0.631 mm (s.d. = 0.274), diameter - 0.0089 mm (s.d. = 0.003), length/diameter ratio - 70, vessel diameter - 0.1425 mm (s.d. = 0.0095) and parenchyma cells - 0.021 mm (0.0047).

Some changes do take place in fiber dimensions during pulping. However, the changes are least important in the kraft process (Rydholm 1965). Fiber dimensions are normally reported for the original wood - the fibers are separated in a way to cause least damage (e.g. delignification with chlorite, cutting into small chips, fibrization by treatment in cold dilute alkali). As mentioned just above, kraft pulping causes least damage to fibers and thus the measurements on pulp fibers can be assumed safely to correspond to the original wood.

The range of fiber length and diameter for hardwoods are reported to be 0.7 - 1.5 mm and 0.015 - 0.025 respectively (Higgins,1969)Phillips et al(1967) have reported and average wood fiber length of 1.04 mm for the mixed mature eucalypt used in their study (E. marginata, E. calophyllaand E. diversicolor). Average length and diameters of two Indian species - E.grandis and E. hybrid are reported to be 0.82, 0.79 mm and 0.014, 0.0122 mm respectively (Srivastava and Mathur, 1964; Unkalkar et al. 1974). The average fiber dimensions of E. tereticornis pulp samples is lessthan the reported value and may be due to the young age (8-10 years) of the species under study. The length diameter ratio of 70 is comparable with the reported value for other species (range: 60-79).

Vessels and parenchyma cells were also observed in the pulp fibers with mean diameters of 0.1425 mm and 0.021 mm respectively. The values are in the range (0.15 - 0.5 mm) reported by (Alger, 1960) for eucalypt kraft pulps. The general range for hardwoods is, however, reported to be 0.02 -0.5 mm and 0.02 -0.2 mm for vessels and parenchyma cells respectively (Rydholm, 1965).

PINE (Pinus roxburghii):

Chemical Composition: Proximate analysis of pine (Pinus roxburghii) is shown in Table 5.2. Extractives constitute 12 per cent of the pine wood meal. Extractive-free pine wood meal contains: lignin - 33.1 per cent (s.d. = 1.213), holocellulose - 66.5 per cent(s.d. = 0.71) (after 6 extractions with acidic sodium chlorite) and pentosans - 9 per cent. The lignin content is slightly higher than the value typical of pines (25 - 30 per cent). The results are compared with the range of chemical compositions of north American and scandinavian pine species and a comparison of these values shows that the chemical composition is almost in the range reported for other species.

Pine wood meal was obtained from irregular shaped wood mainly from branch zone of main stem and reaction wood. These zones normally have more lignin than the main stem. This may be possible reason for getting higher lignin content.

<u>Basic wood density:</u> Average density of Pinus roxburghii chips (air dry) measured as weight of oven-dry chips per unit volume of air dry chips was found to be 0.56 g cm^{-3} and lies in the reported range for pines (0.36 - 0.56, o.d. weight/green volume). Shrinkage of air-dry chips will give slightly higher basic density as is observed in this case also. Basic wood density of Pinus khasaya is reported in the range:0.38-0.50 gm cm^{-3} (Bhaumic and Ghosh, 1975).

<u>Fiber Dimensions:</u> Two unbeaten pulp samples from experiments numbers P-45,-51 of the main design were used for the measurement of fiber dimensions. The results reported are the number average of 254 observations (20 slides containing 12-15 fibers each). These values are: Length -5.0 mm (s.d. = 1.3), diameter - 0.046 mm (s.d. = 0.014), wall thickness - 12.63 μm (s.d. = 2.47), lumen diameter - 19.81 μm (s.d.=5.41) and length/diameter ratio - 110 and agree well with the values reported by Bhat and Singh (1955) for the same species. (length - 4.8 mm; diameter -0.051 mm; length/diameter ratio -94; species -Pinus longifolia Roxb.).

Average fiber length of most commercially important north American pine species is around 3.5 mm with length/diameter ratio of 80-100. Certain pines (longleaf and short leaf Loblolly pines), Douglas fir and western hemlock also have a higher average fiber length (4-6 mm). Pinus roxburghii pulp fibers also have a higher wall thickness (12.6 μm)

compared to most pines (3-5 μm). Reaction wood fibers have higher wall thickness and may be twisted wood (P. roxburghii) is similar to reaction wood. Nevertheless, some softwoods are reported to have wall thickness as high as 15 μ m; European beach (Fagus silvatica) is an example (Rydholm, 1965). Pinus khasaya has been reported to have a wall thickness of 6.14 μm.

APPENDIX III

BEATING CHARACTERISTICS OF EUCALYPT AND PINE KRAFT PULPS

Eucalypt Kraft Pulps: The development of strength characteristics of unbleached eucalypt kraft pulps was studied at different freeness levels (°SR) using a Valley beater for refining. Beating curves were obtained for the freeness range of 18-80 °SR corresponding to beating period upto 60 min, Figure A.1. The pulp hand sheets were conditioned and tested for tear index, burst index, tensile index and folding endurance, and the results are summarized in Figures A.1 - A.6. The beating characteristics obtained for eucalypts are similar to the behaviour normally observed with hardwood kraft pulps and showed the following trends:

1. Freeness levels of 20 and 40°SR are obtained after beating for 10 and 30 min respectively.
2. Tear index shows a maximum (8.2) at 50 °SR and is about 7.5 at 40 °SR.
3. Burst index develops rapidly with beating to about 4 at 40 °SR.
4. Tensile index develops rapidly with beating upto 40°SR and the rate declines with further beating.
5. Folding endurance improves only at freeness levels above 40 °SR.

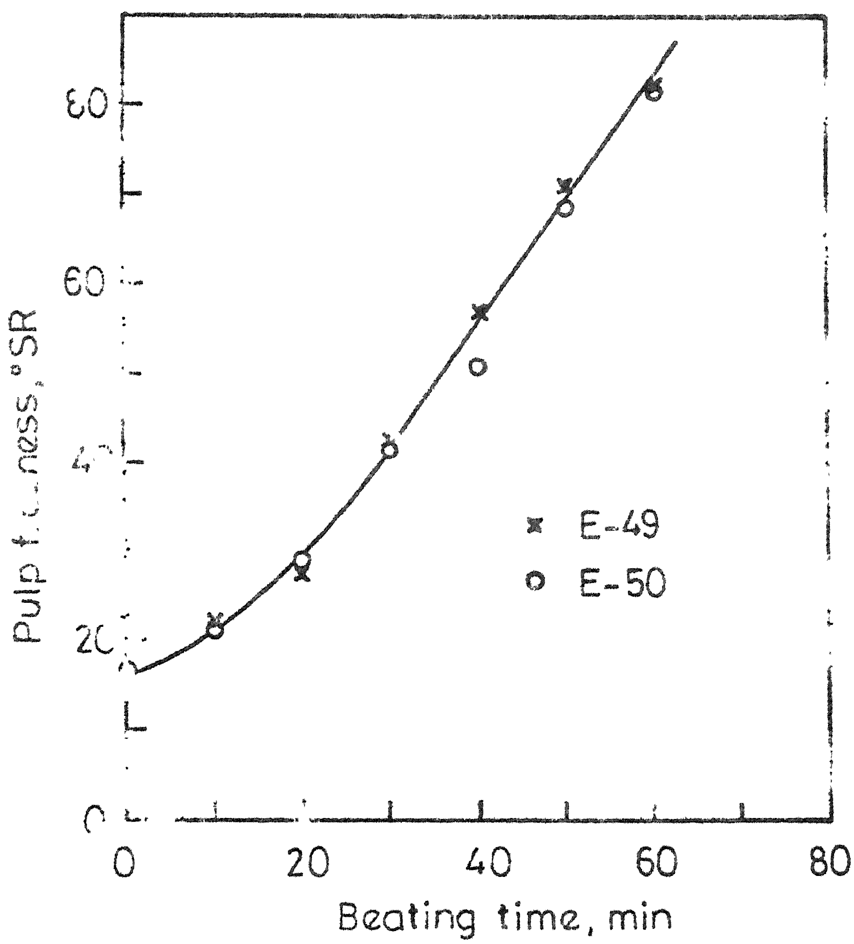


Fig. A- - Beating characteristics of eucalypt
kraft pulp.

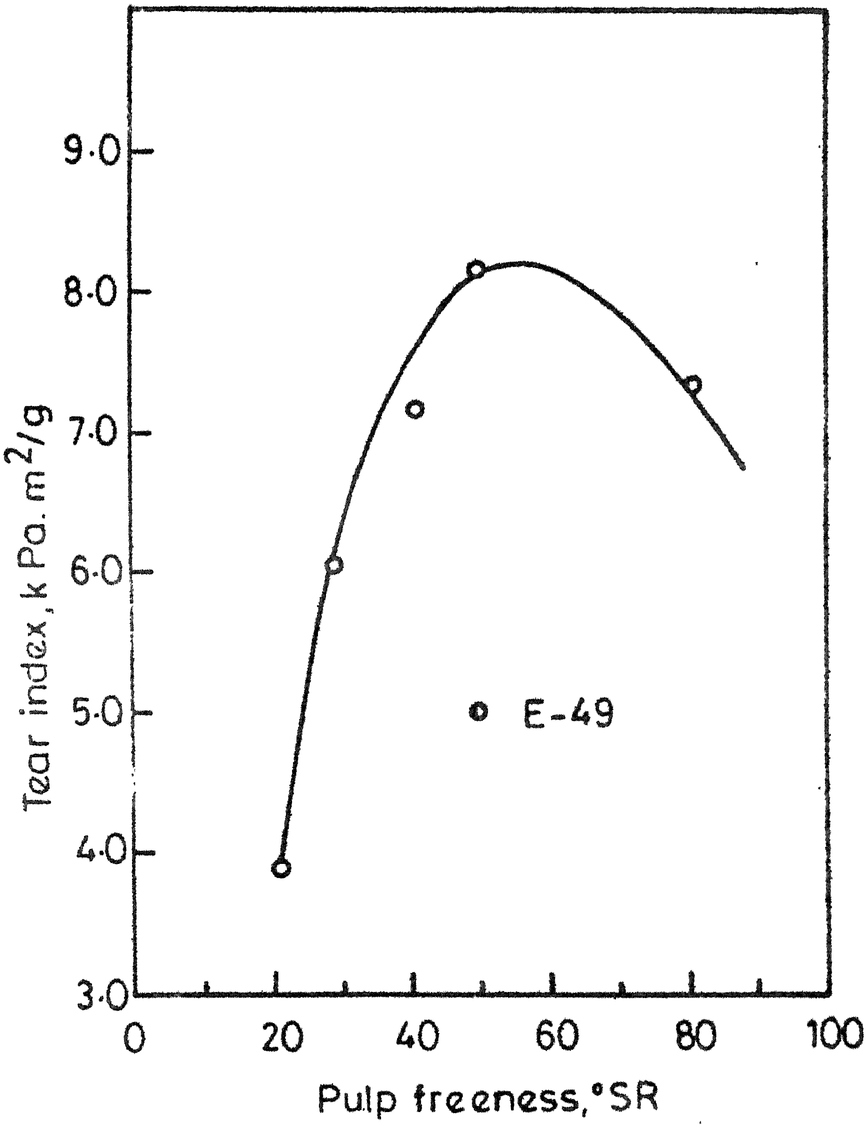


Fig. A·2 - Variation of tear index with freeness for eucalypt pulp.

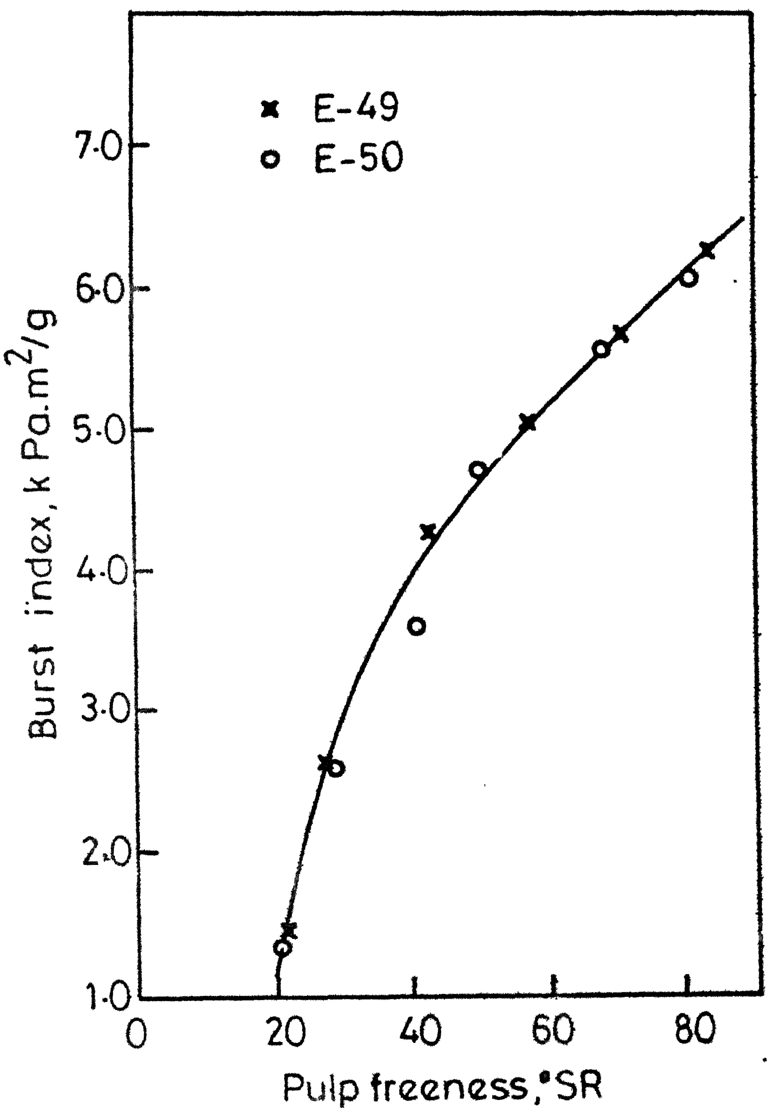


Fig. A-3 - Variation of bust index with pulp freeness for eucalypt pulp.

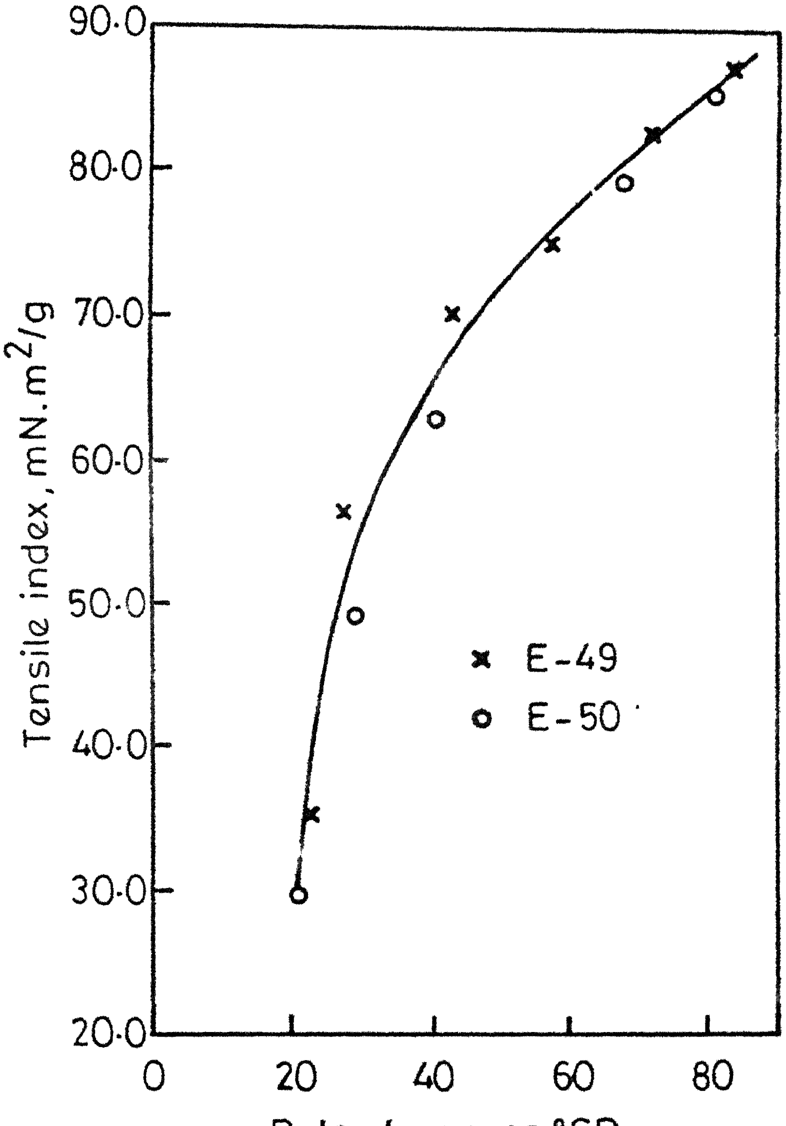


Fig.A·4 - Variation of tensile index with pulp freeness for eucalypt pulp.

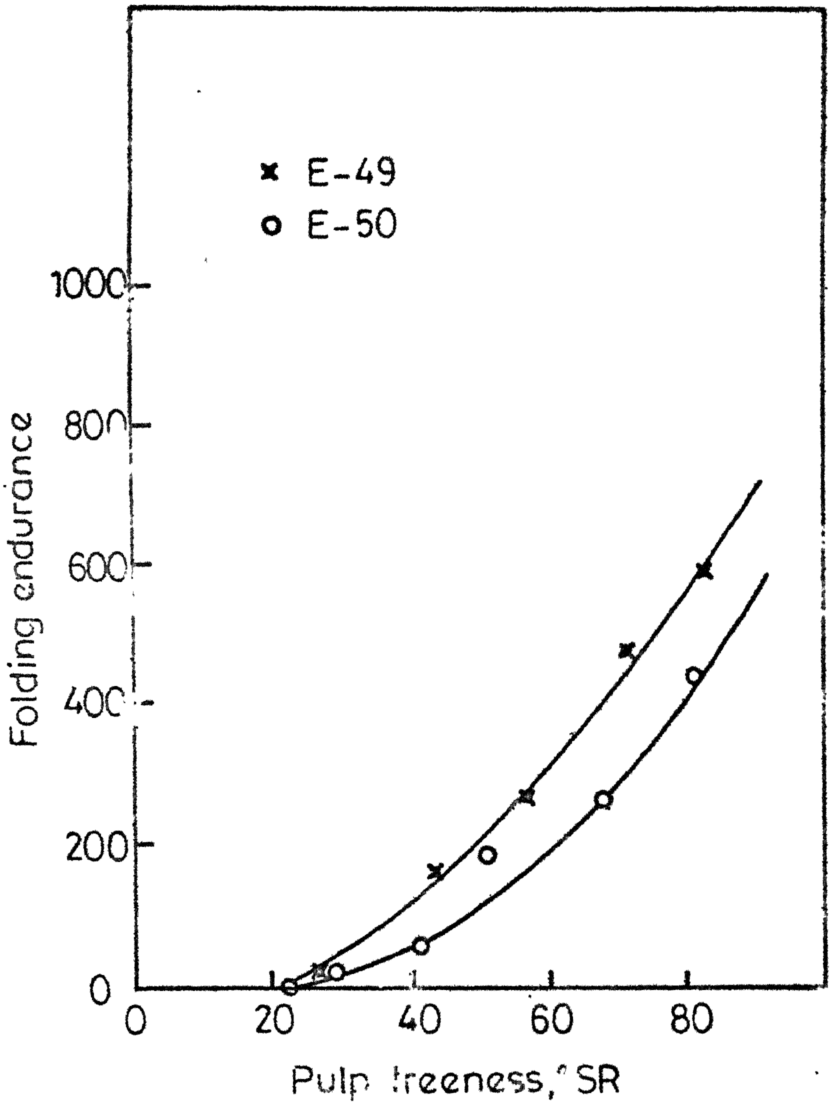


Fig. A-5 - Variation of folding endurance with pulp freeness for eucalypt pulp.

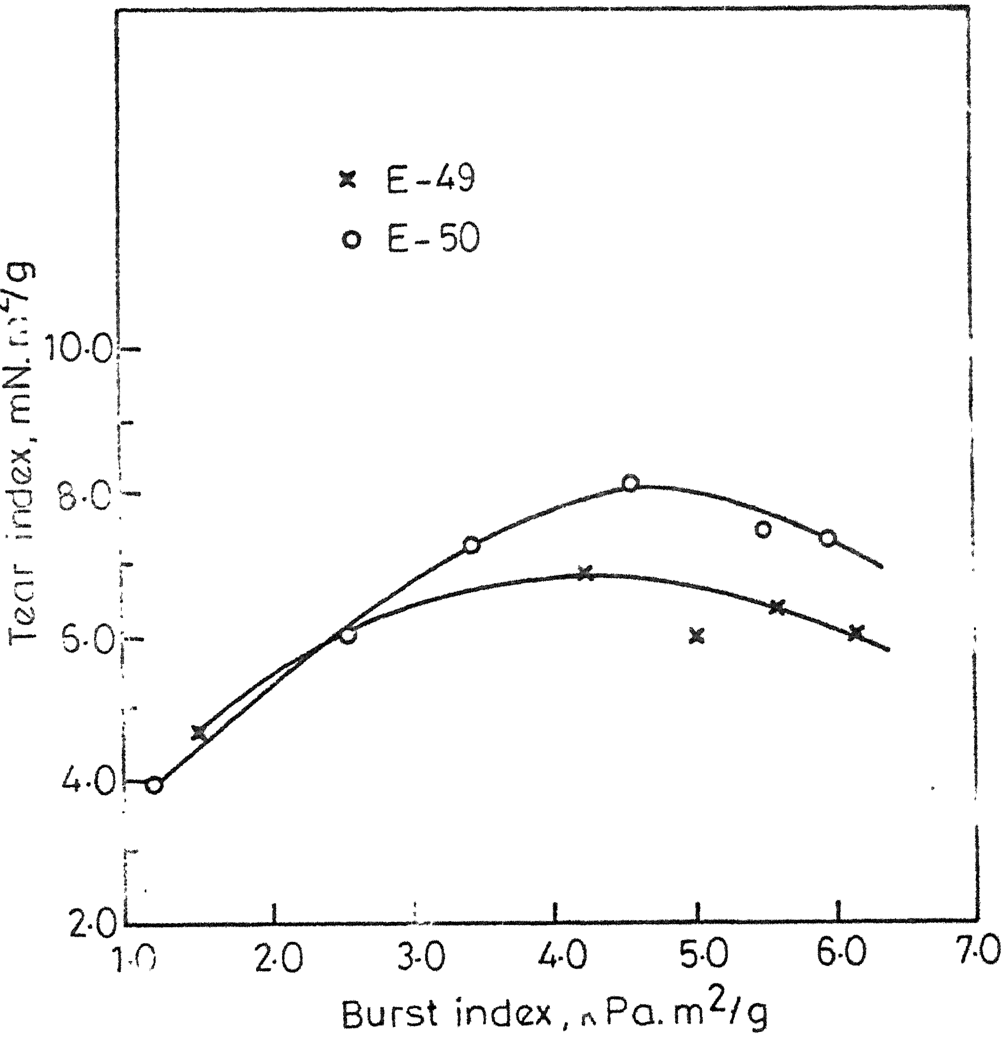


Fig. A·: -Correlation between tear index and burst index for eucalypt pulp.

6. The correlation of tear index and burst index shows that the maximum tear index obtainable is 8.2 with burst index of 4.5.

Thus the eucalypt kraft pulps must be beaten to 40 °SR to develope the potential strength properties - tear, burst, tensile and folding endurance.

<u>Pine Kraft Pulps</u>: Beating characteristics of unbleached pine kraft pulp samples also were determined in the same manner and the results are graphically presented in Figures A.7 - A.12. The graphs in Figures A.7-A.12 lead to the following observations.

1. Freeness levels of 14, 16 and 40 °SR are obtained after beating for 10, 30 and 60 min.respectively.
2. Slight beating (15-20 °SR) gives a high tear index and decreases rapidly past 20 °SR and reaches a value of 15 around 40 °SR.
3. Burst index develops well upto 40 °SR and reaches a steady value above 40 °SR.
4. Tensile index increases rapidly until 40 °SR and reaches a constant value above 50 °SR.
5. Folding endurance plots show a maximum at about 40 °SR and decreases at higher freeness levels.
6. Burst index increases while tear index decreases with beating. Consequently the tear index - burst index correlation shown in Figure A.12

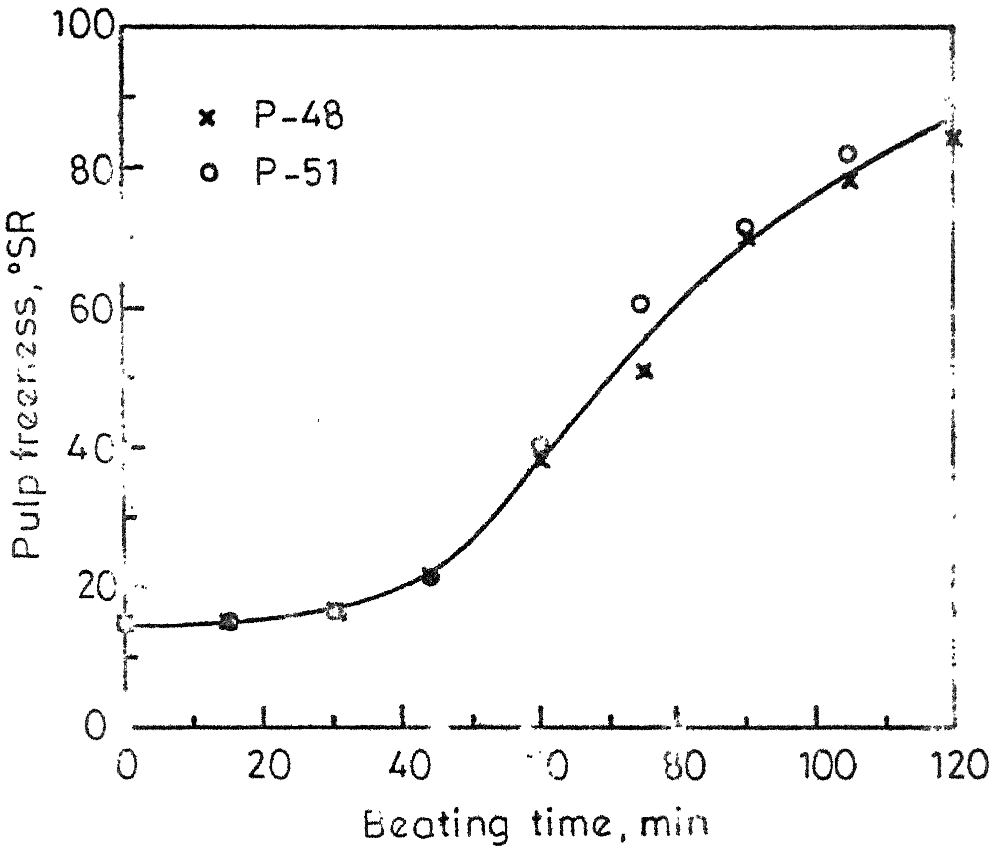


Fig. A-7 - Beating characteristics of pine kraft pulp.

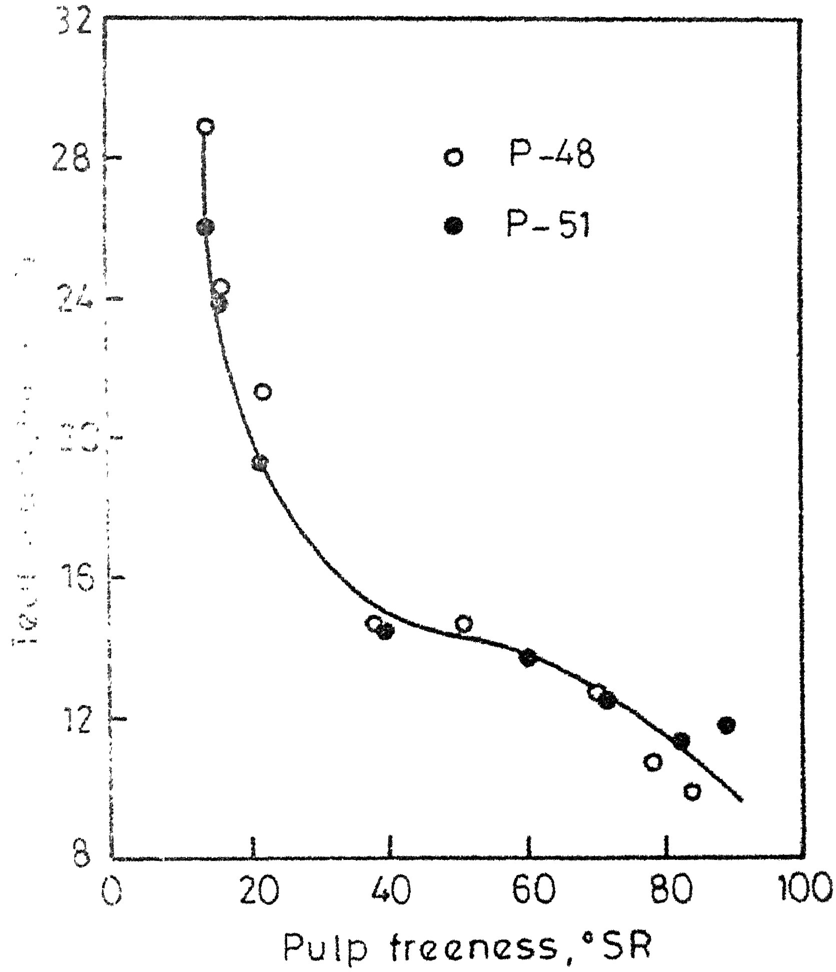
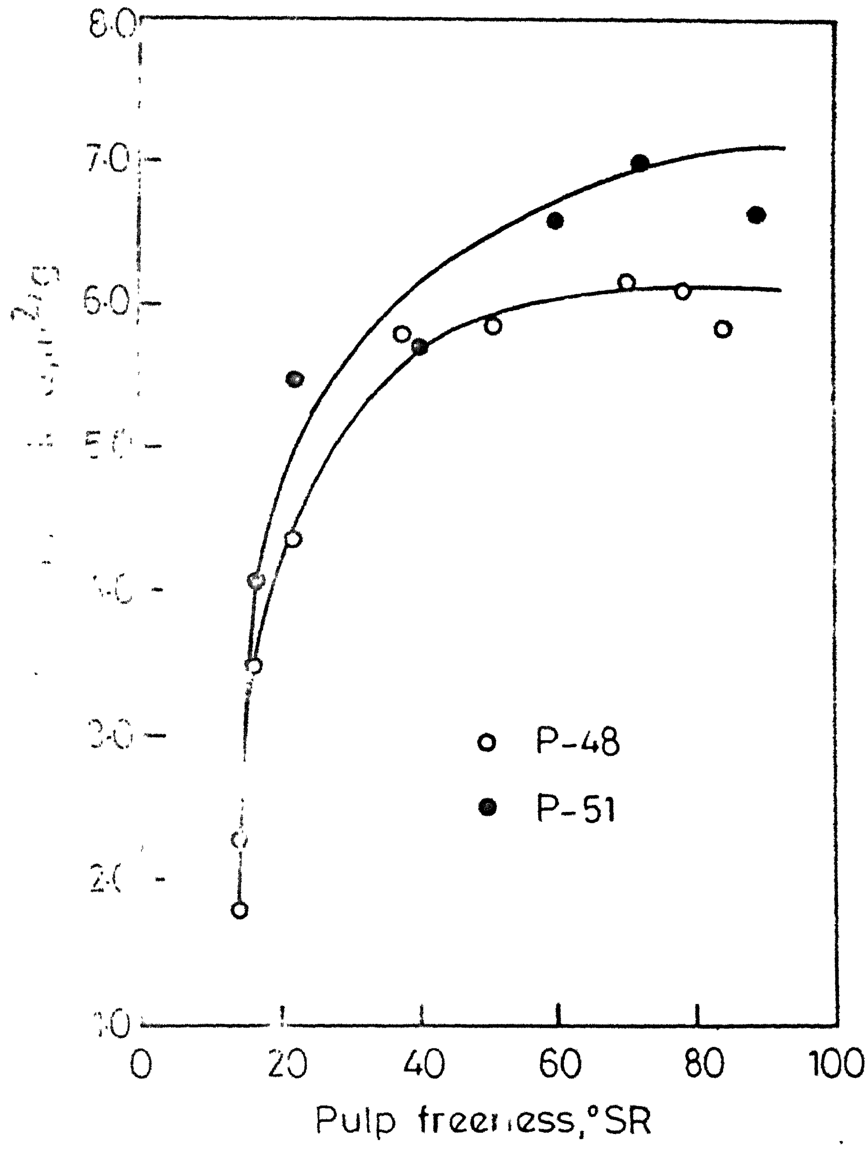


Fig. A-8 - Variation of tear index with freeness for pine kraft pulp.



... -Variation of burst index with freeness for ... ulp.

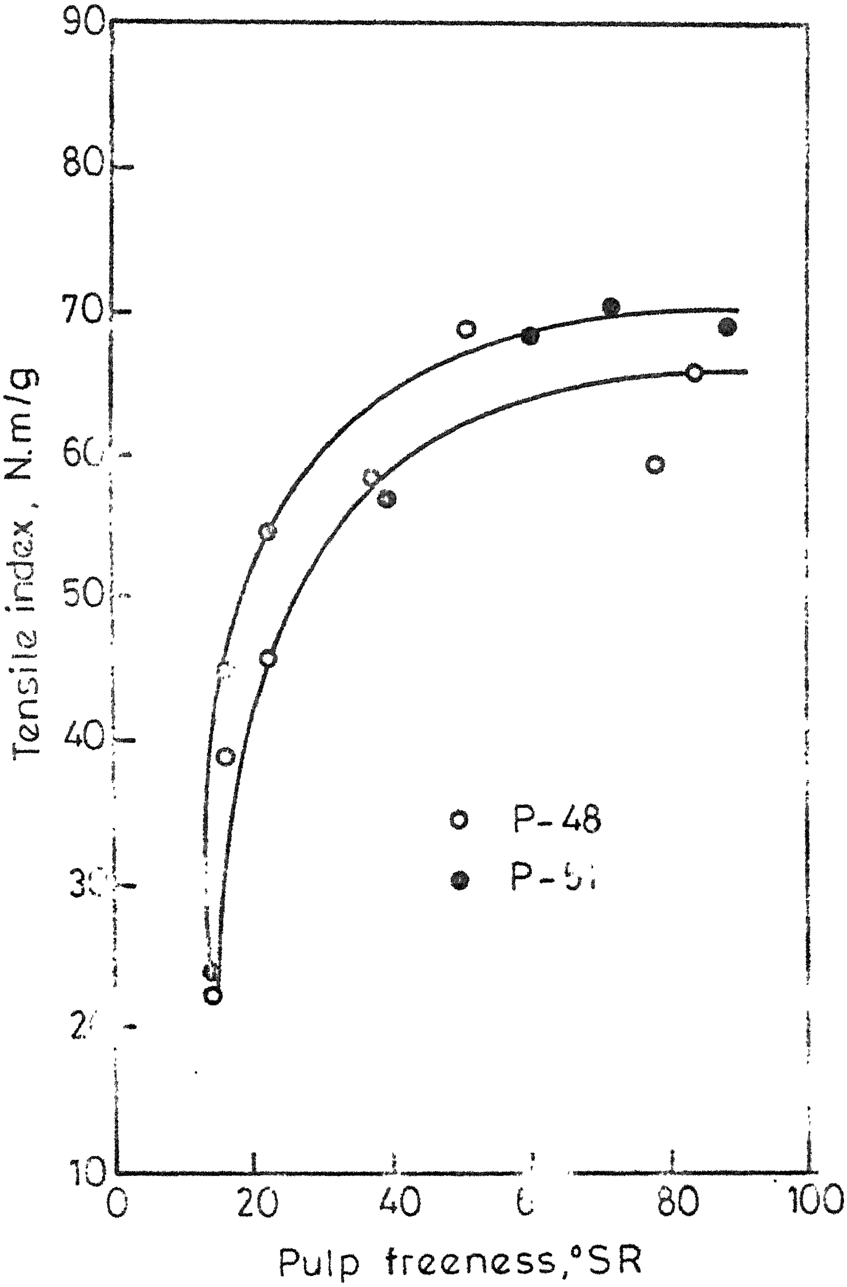


Fig.A-10-Variation of tensile index with pulp freeness for pine pulp.

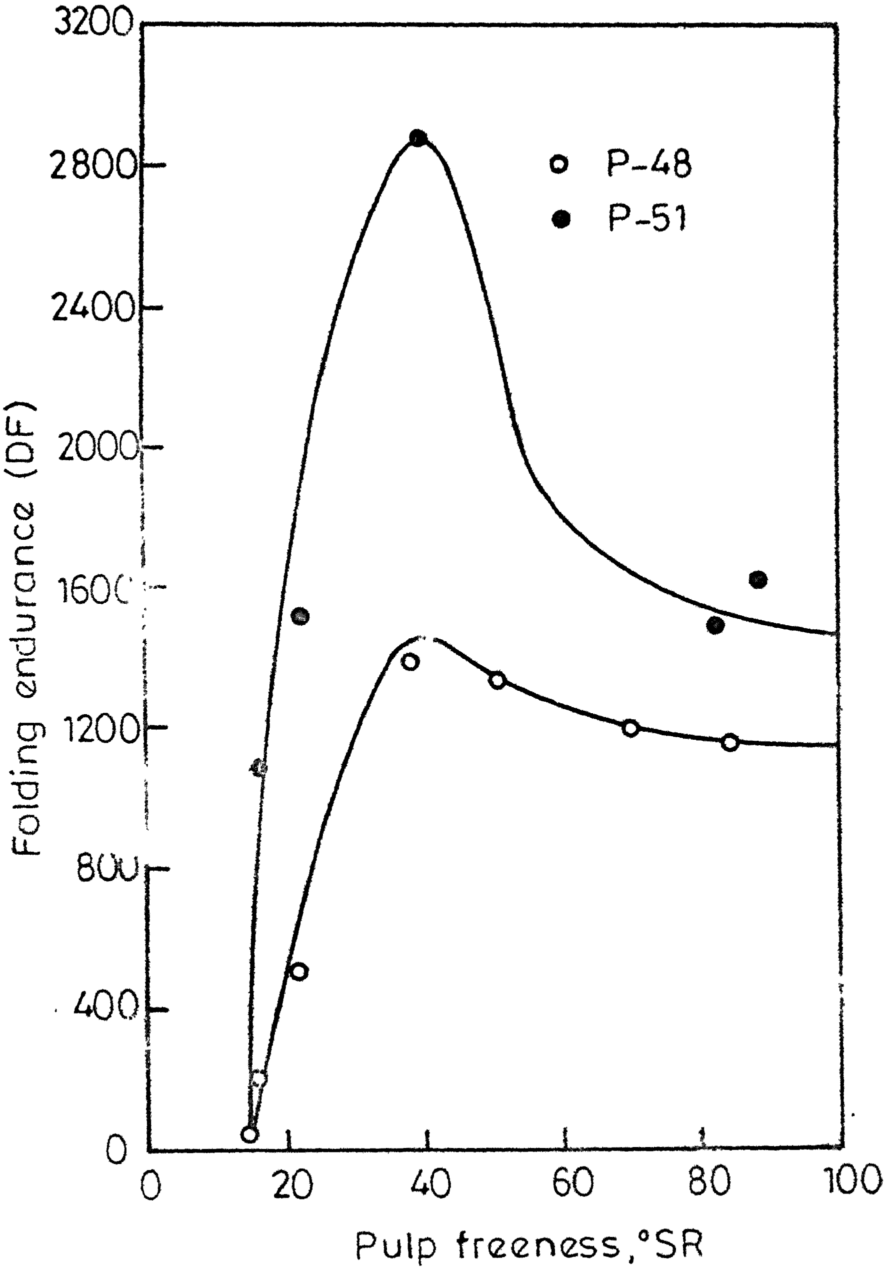


Fig. A-11-Variation of folding endurance with freeness for pine pulp.

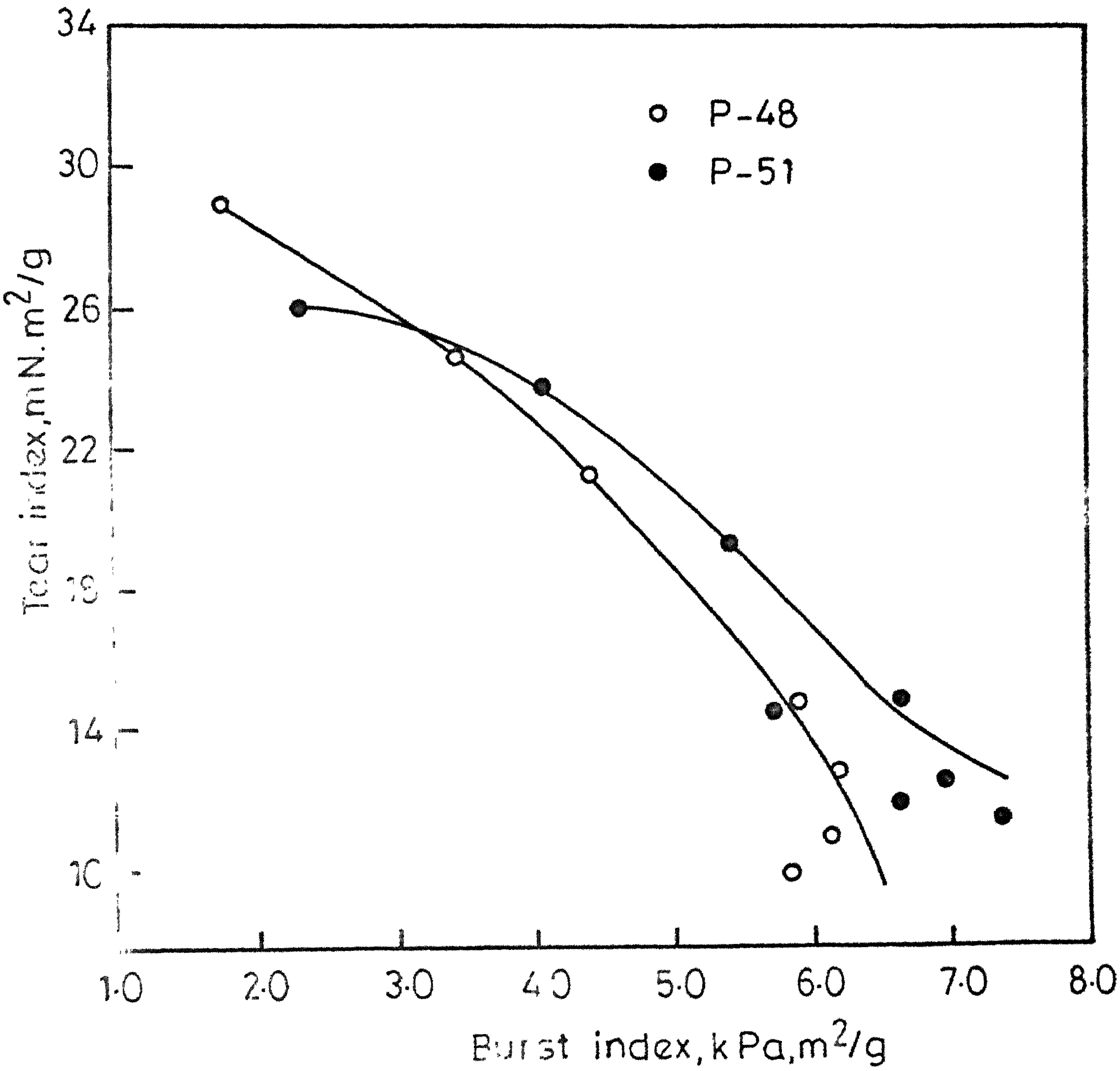


Fig. A·12 - Correlation of tear index and burst index for pin pulp.

shows a continuous decrease of tear index with burst index.

The above data shows that slight beating of pine (15-20 °SR) would give good tearing resistance and the other strength properties - burst, tensile and folding endurance develope only on beating to about 40 °SR. A comparison with eucalypt pulp, (at 40 °SR) shows that pine pulp has superior tearing resistance (14 vs 7-8), better bursting strength (5.5 - 6.5 vs 4.0), superior folding endurance (1400-3200 vs 50-175), and both have similar tensile strength values.

Thus both eucalypt and pine kraft pulps must be beaten to 40 °SR to develope the potential strength properties - tear, burst, tensile and folds. The pulps obtained from all the experiments of this study are beaten to 40 °SR for the determination of strength properties of the pulp handsheets.

APPENDIX IV

YATES'S ALGORITHM FOR A 2^3 FACTORIAL DESIGN

The analysis of the results of factorial experimental designs give the main effect of each factor (process variable) and the interaction effects between the different variables on the overall response. The main effect of a variable measures its average effect over the experimental range of all the other variables. Yates's algorithm is a quick method of calculating these effects.

The experimental design is arranged in a standard manner as shown in Table 3.2 for a 2^3 design. Table A-1 shows a standard form of table for Yates's algorithm in which data for pine pulp yield (Table 6.3) have been arranged systematically. For simplicity, the variables are denoted by the letters A, B and C for chemical charge, temperature and time respectively. The column entitled 'treatment combination', represents the standard notation indicating the actual levels used for the experiments in a two level design. Thus, presence of a small letter (a,b or c) means that the variable is at its higher level and its absence signifies that the variable is at the lower level. Thus, treatment combination (1) means all the three variables are at the lower level; treatment combinations a, b, c refer to higher level of A,B, and C and ab, ac,bc refer to the higher levels

total yield by 0.93 per cent. Similarly the average effect of temperature (165–175°C) increase is to decrease the yield by 1.9 per cent. The average effect of an increase in pulping time (60–90 min.) is a decrease in yield by 0.41 per cent. Chemical charge and temperature show an interaction effect decreasing the yield by 0.3 per cent.

The statistical significance of the calculated effects and interactions must be determined using an estimate of the possible experimental error, obtained from replicate determinations. In the absence of replicate experiments, the significance of the factors can also be determined by constructing variance tables and the sum of squares of the interaction terms are taken as an indication of error variance (Davies, 1967; Box et al. 1978). Sum of squares for a factor or interaction is obtained by squaring the corresponding element in column(3) of Table A.1 and dividing by 8 (except for the grand average). All these sums of squares have only one degree of freedom and hence the mean squares (M.S.) will be equal to the sum of squares. The mean squares are used for the analysis of variance in Table A.2.

The sum of squares of the four interaction terms – AB, AC, BC and ABC is 2.841 with 4 degrees of freedom. The mean square for error variance is then $\frac{2.841}{4} = 0.7102$. The variance ratio is the ratio of mean square to the error variance for each effect or interaction. The variance ratios

are given in the last column of Table A.2. F-ratio from the statistical table (Himmelblau, 1967) at 95 per cent confidence level and at 1 and 4 degrees of freedom is ($F_{0.95}$ (1,4) = 7.7086). This value is compared with the value of variance ratios in the table. It is seen that only the variance ratio 10.245 corresponding to the temperature change is higher than the tabulated value of F-ratio. Alternatively, mean square necessary for a factor to be significant is given by (M.S.) = F-ratio x error variance (7.7086 x 0.7102 = 5.492), which also shows the significant influence of temperature. Hence it is concluded that in the experimental range studied, only the pulping temperature has significant effect on yield.

TABLE A-1: KRAFT PULPING OF PINE: STATISTICAL ANALYSIS OF DATA FOR PULP YIELD

CALCULATION OF EFFECTS AND MEAN SQUARES BY YATES'S METHOD

Expt.No.	Treatment combination[a]	Response Total yield y	Yates's analysis 1	Yates's analysis 2	Yates's analysis 3	Effect	Sum of squares or Mean square = $(3)^2/8$
P-1	(1)	50.83	100.01	194.48	387.31=Total	48.41	-
P-2	a	49.18	94.47	192.83	-3.73= 4A	-0.933	1.739
P-3	b	47.66	97.47	-2.50	-7.63= 4B	-1.908	7.277[b]
P-4	ab	46.31	95.36	-1.23	-1.21= 4AB	-0.303	0.183
P-5	c	48.54	-1.65	-5.54	-1.65=4C	-0.413	0.340
P-6	ac	48.93	-0.85	-2.11	1.27= 4AC	0.318	0.201
P-7	bc	48.49	0.39	0.80	3.43= 4BC	0.858	1.470
P-8	abc	46.87	-1.62	-2.01	-2.81= 4ABC	-0.703	0.987

A - chemical charge

B - temperature

C - time

b significant at 95 per cent confident level.

TABLE A.2: KRAFT PULPING OF PINE
2^3 FACTORIAL DESIGN

ANALYSIS OF VARIANCE FOR TOTAL PULP YIELD

Sources of variations	Sum of squares (S.S.) Table A-1)	Degree of freedom (d.f.)	Mean square $M.S. = \frac{S.S.}{d.f.}$	Variance ratio $= \frac{M.S.}{\text{Error variance}}$
A-chemical charge	1.739	1	1.739	2.448
B-temperature	7.277	1	7.277*	10.245*
C-time	0.340	1	0.340	0.478
AB-chem.-temp.	0.183	1	0.183	0.257
AC-chem-time	0.201	1	0.201	0.283
BC-temp.-time	1.470	1	1.470	2.069
ABC-chem-temp-time	0.987	1	0.987	1.389
Error variance (sum of interaction terms)	2.841	4	0.71025	

$F_{0.95}$ (1,4) = 7.7086; Mean square for significance = 7.7086 x 0.7125 = 5.492

*Significant at 95 per cent confidence level

Alternatively: Standard error in yield determination (from central point experiments in main design) = 1.042 (d.f.=8)

Error variance = 1.0857

$F_{0.95}$(1,8) = 5.32; M.S. = 5.32 x 1.0857 = 5.776

$F_{0.90}$ (1,8) = 3.46; M.S. = 3.46 x 1.0857 = 3.7567

Since mean square (M.S.) for temperature is greater than the mean square for significance at 95 per cent confident level, temperature is considered significant.

APPENDIX V

YATES'S ALGORITHM FOR A 2^2 FACTORIAL DESIGN

The experimental data of screened pulp yield are analyzed by Yates's algorithm and the results are summarized in Table A.3. The effects of time - to - temperature and pulping temperature were studied using a simple 2^2 factorial design (4 expts.).

The average effect of time-to-temperature (60-120 min) is to increase the screened yield by 1.9 per cent while the average effect of increasing pulping temperature (160-170°C) is a decrease in screened yield by 0.8 per cent. The inter-action effect shows that if both the time-to-temperature and temperature are at the higher level, the result will be a further decrease in screened yield by 0.6 per cent. Thus it would be adivisable to increase the time-to-temperature and to pulp at a lower temperature level for maximum screened pulp yield.

To determine the statistical significance of the calculated effect, it is assumed that the error variance between replicated runs (E-1, E1R and E-4, E-4R) will give an estimate of the total variability affecting runs made at different experimental conditions (Box et al. 1978).

Error variance of the two experiments repeated at identical conditions is given by the equation

$$s_i^2 = \frac{d_i^2}{2}$$

where d_i - difference between the two responses (yields) for the repeated experiments. The overall variance is calculated by the equation

$$s_y^2 = \frac{\sum_{i=1}^{k} s_i^2}{k} = \frac{s_1^2 + s_2^2}{2}$$

where k - number of experiments repeated (=2)

The estimated variance of the effect is calculated by the formula

$$s_v^2 = \frac{s_y^2}{N}$$

where N - number of experiments in the design (=4)

The significance of the main effects and interactions is tested by constructing the confidence interval for the effects by the following formula

$$\text{Effect} \pm t_{0.05} \sqrt{\text{Estimated variance of the effect}}$$

Students' t value at 95 per cent confidence level (5 per cent significance) and 2 degrees of freedom (one degree of freedom for each replicated test) is equal to 2.92 (Himmelblau, 1967). If absolute value of the main effects and interactions is found to be larger than the confidence interval calculated by the above formula, the effect is considered to be significant.

Sample calculations for the estimation of error variance and confidence interval for screened pulp yield is

also given in Table A.3. The confidence interval for screened yield is $\pm$ 0.286 and thus both the main effects and interaction are significant.

TABLE A-3: EFFECT OF TIME-TO-TEMPERATURE AND TEMPERATURE IN KRAFT PULPING OF EUCALYPTS

ANALYSIS BY YATES'S ALGORITHM FOR SCREENED PULP YIELD

Expt. No.	Treatment combination	Algorithm: Screened pulp yield, % y	Algorithm: (1)	Algorithm: (2)	Estimate of effect	Identification[a]	Confidence interval
E-1	(1)	46.50	95.47	189.31	47.33	Average	-
E-2	a	48.97	93.84	3.75	1.88	$A = t_h$	1.88 ± 0.286
E-3	b	46.28	2.47	-1.63	-0.82	$B = T$	-0.82 ± 0.286
E-4	ab	47.56	1.28	-1.19	-0.60	$AB = t_h x T$	-0.60 ± 0.286

a A-time-to-temperature, B-temperature

Estimation of confidence interval:

E-1 yield = 46.50 Error variance $s_1^2 = 0.00098$ with 1 d.f.

E-1R yield = 46.36

E-4 yield = 47.56

E-4R yield = 47.17 Error variance $s_2^2 = 0.0760$ with 2 d.f.

Experimental error variance (pooled), $s_y^2 = \frac{s_1^2 \; s_2^2}{2} = 0.0385$

Estimated variance $s_v^2 = \frac{s_y^2}{N} = \frac{0.0385}{4} = 0.009625$

Students' t value at 95 per cent confidence level and 2 degrees of freedom

$$t_{0.95,2} = 2.92$$

Confidence interval: $\pm\, t_{0.95,2} \sqrt{\text{Estimated variance}}$

$\pm\, 2.92 \sqrt{0.009625}$

$\pm\, 2.92 \times 0.0981$

$\pm\, 0.286$

APPENDIX VI

ANALYSIS OF EFFECTS FOR A 3x2 FACTORIAL DESIGN

The effects of chemical charge and chip thickness were studied using a simple 3x2 factorial design (6 experiments). The experimental data of total pulp yield are analyzed by Yates's algorithm and the results are illustrated in Table A.4. The entries in columns give total pulp yield at constant chip thickness and the entries in rows correspond to yield at constant chemical charge. The columns or rows entitled 'Total' and 'Mean' give total and average yield respectively at a constant chemical charge/chip thickness. Thus 48.7 per cent is the average yield for the three experiments conducted with 2.5 mm thick chips while 48.55 per cent average yield is obtained for pulping with 17 per cent chemical charge.

The linear effect of chemical charge is calculated by subtracting the mean yield at 15 per cent chemical charge from the mean yield at 17 per cent chemical charge and dividing the result by 2. The quadratic effect of chemical charge is the sum of mean yields at 15 per cent and 17 per cent chemical charges minus twice the mean yield at central point condition of chemical charge (16 per cent) and dividing the whole by 2. The linear effect of chip thickness is simply the difference of mean yields at the two levels of chip thickness.

The main linear effect of chemical charge is to decrease pulp yield by 1 per cent with an increase in chemical charge of 1 per cent. Positive quadratic effect of chemical charge shows that low level of chemical charge has a pronounced decreasing effect on yield. The increase in chip thickness from 2.5 to 3.5 mm increases total yield by 0.9 per cent.

TABLE A-4: INFLUENCE OF CHEMICAL CHARGE AND CHIP THICKNESS ON THE KRAFT PULPING OF EUCALYPT

ANALYSIS OF EFFECT BY YATES'S ALGORITHM FOR TOTAL PULP YIELD

Chemical charge, %		Chip thickness, mm				Total	Mean
Level	Actual value	Level: Value:	-1 2.5		2 3.5		
-1	15	(E-11)	49.6	(E-14)	51.5	101.10	50.55
0	16	(E-12)	48.1	(E-15)	48.5	96.60	48.30
+1	17	(E-13)	48.4	(E-16)	48.7	97.1	48.55
Total			146.10		148.70	294.8	
Mean			48.70		49.57		

Numbers in parenthesis show experiment nos.

$$\text{Linear effect of chemical charge} = \left(\frac{48.55-50.55}{2}\right) = -1.00\%$$

$$\text{Quadratic effect of chemical charge} = \left(\frac{48.55+50.55-2\times 48.30}{2}\right)$$

$$= 1.25\%$$

$$\text{Main effect of chip thickness} = (49.57-48.70) = 0.87\ \%$$

APPENDIX VII

FORTRAN PROGRAM FOR YATES'S ALGORITHM

```
-----------------------------------------------------------------------
K R A F T   P U L P I N G   O F   P I N E(P.roxburgii V latifolia)
-----------------------------------------------------------------------
The five pulping variables are (Design order):
   1. Chemical charge,%AA as Na2O              16 - 19
   2. Temperature, C                          165 - 175
   3. Time, min.                               60 - 100
   4. Sulfidity, %                             20 - 30
   5. Liquor-to-wood ratio                    3.5 - 4.0
The half fraction of the 2**5 factorial design [2**(5-1)] was
constructed as follows:
1. A full 2**4 design was written for the four variables 1,2,3,4
2. The column of sign for the 1234 interaction was written, and
   these were written to define the levels of variable 5.
   Thus we make 5 = 1234;
   This relation is called the generator of the design.
3. The effects are calculated using Yates's algorithm for
   4 variables in the standard order.
4. the calculated effects are associated with their appropriate
   aliases to determine the effect of 5 variables and the two

   factor interactions :-
                  123  = 45
                  124  = 35
                  134  = 25
                  234  = 15
                 1234  =  5
The variables are identified in the following order:
       Chemical charge        (1)
       Temperature            (2)
       Sulfidity              (3)
       Liquor-toOwood ratio   (4)
       Time                   (5)
The mean value and interaction terms are identified as:
       Mean value                   0
       Chem.Temp. interaction      12
       Temp. Time interaction      25   etc.
-----------------------------------------------------------------------
```

```
C ----------------------------------------------------------------
C        YATES'S  ALGORITHM FOR THE CALCULATION OF EFFECTS AND
C              INTERACTIONS FOR A 2-LEVEL FACTORIAL DESIGN.
C ----------------------------------------------------------------
C     Description of Parameters:
C     N        Total number of experiments (=2**k).
C     Y        Vector of responses (Experimental results).
C     YY       Intermediate vector.
C     NVAR     Number of factors(variables) in the design(k).
C     ENTRY    Matrix of entries generrated by Yates's algorithm.The
C              number of columns in ENTRY is equal to the number of
C              factors (k) in the design.
C     EFFECT   Main effects and interactions obtained by dividing the
C              entries in column k by N/2, except the first entry,
C              which is divided by N.
C     IDENT    Identification of the main effects and interactions.
C ----------------------------------------------------------------
      DIMENSION Y(16) , YY(16) , ENTRY(16,4) , EFFECT(16) , IDENT(16)
      NVAR = 4
      N    = 16
      READ(1,*) , (IDENT(I),I=1,N)
 10   READ(1,*) , (Y(I),I=1,N)
      DO  15  I = 1,N
 15   YY(I) = Y(I)
      DO  100  J = 1,NVAR
      NHALF = N/2
      DO  50  I = 1,N
      IF(I .GT. NHALF)  GO TO 40
      II = 2*I
      ENTRY(I,J) = YY(II) + YY(II-1)
      GO TO 50
 40   II = 2*(I-NHALF)
      ENTRY(I,J) = YY(II) - YY(II-1)
 50   CONTINUE
      DO  60  I = 1,N
 60   YY(I) = ENTRY(I,J)
 100  CONTINUE
      EFFECT(1) = ENTRY(1,NVAR)/N
      DO  120  K = 2,N
 120  EFFECT(K) = ENTRY(K,NVAR)/NHALF
      PRINT 121
 121  FORMAT(5X,'YATES ALGORITHM',3X,'KRAFT PULPING OF PINE',3X,
     1'FRACTIONAL FACTORIAL DESIGN 2(5-1)',//)
      PRINT 122
 122  FORMAT(30X,'SCREENED PULP YIELD',//)
      PRINT 123
 123  FORMAT(5X,'---------------------------------------------------
     1----------------------',/)
      PRINT 124
 124  FORMAT(/,5X,'Exp.',3X,'Response',5X,'(1)',7X,'(2)',7X,'(3)',7
     1X,'(4)',5X,'Estimate'2X,'Ident',/)
      PRINT 123
      DO  125  I = 1,N
      PRINT 126, I , Y(I) , (ENTRY(I,J),J=1,NVAR) , EFFECT(I),IDENT(I
 125  CONTINUE
 126  FORMAT(5X,I2,2X,6F10.2,I7,/)
      PRINT 123
      STOP
      END
C ----------------------------------------------------------------
```

APPENDIX VIII

FORTRAN PROGRAM FOR LINEAR REGRESSION ANALYSIS

```
      -----------------------------------------------------------------
            L I N E A R   R E G R E S S I O N   A N A L Y S I S
C     -----------------------------------------------------------------
C     This program uses Subroutine STREG for calculating Beta vector
C       and other statistical parameters for linear regression.
C     MV  actual number of independent variables(explicit) - x1,...,x5
C     M   total number of variables (Dependent+Independent(explicit+
C         implicit))  eg.,(x1,x2,...,x11,x22,...,x12,x13,...,x45).
C         also equal to the total number of parameters to be estimated
C         eg.,(b0,b1,b2,...,b5,b11,b22,....,b55,b12,b13,...,b45).
C     N   total number of observations on each variable.
C     The first variable is taken to be the dependent variable vector
C         eg.,   X(1,J) = y.
C     Only the design matrix x1,...,x5 is read, the implicit varibles
C         x11,....x45 are computed in the main program.
C     -----------------------------------------------------------------
C        Main Program for Linear Regression :
      DIMENSION X(50,100),XBAR(50),S(50,50),A(50,50),R(50,50)
      DIMENSION B(50),YHAT(100),YRES(100),SER(50)
      PRINT 1
 1    FORMAT(10X,'STATISTICAL REGRESSION ANALYSIS - LEAST SQUARE METH(
     1D'//)
      READ(1,*),M,N,MV
      DO 10 I=1,MV
 10   READ(1,*),(X(I,J),J=1,N)
C       Transformations (Implicit variables calculated from explicit
C                            variables) are added here :
C
      DO 15 J=1,N
C       These parameters are the square and interaction terms in the
C         general second order model for the
C           K R A F T   P U L P I N G   O F   E U C A L Y P T
C
       X(7,J) = X(2,J)**2
       X(8,J) = X(3,J)**2
       X(9,J) = X(4,J)**2
       X(10,J)= X(5,J)**2
       X(11,J)= X(6,J)**2
       X(12,J)= X(2,J)*X(3,J)
       X(13,J)= X(2,J)*X(4,J)
       X(14,J)= X(2,J)*X(5,J)
       X(15,J)= X(2,J)*X(6,J)
       X(16,J)= X(3,J)*X(4,J)
       X(17,J)= X(3,J)*X(5,J)
       X(18,J)= X(3,J)*X(6,J)
       X(19,J)= X(4,J)*X(5,J)
       X(20,J)= X(4,J)*X(6,J)
       X(21,J)= X(5,J)*X(6,J)
 15    CONTINUE
       CALL STREG(M,N,X,XBAR,S,A,AA,B,SEE,YHAT,YRES,R2,F,SER,SSE)
       CALL CORR(M,S,R)
       M1=M-1
 16    CONTTNUE
       GO TO 57
```

```
C          Skip to statament 57 if inverse x*x  and the correlation
C             matrix are not needed.
           PRINT 22
22         FORMAT(//,5X,'INVERSE OF X*X IN DEVIATION FORM')
           DO 23 I=1,M1
23         PRINT *,  (A(I,J),I,J,J=1,M1)
24         FORMAT(1X,5(5(5X,F10.5,'(',I2,',',I2,')',2X),/))
           PRINT 45
45         FORMAT(5X,'CORRELATION MATRIX {ZERO IS DEPENDANT VARIABLE}')
25         CONTINUE
           DO 50 I=1,M
50         S(I,I)=SQRT(S(I,I)/FLOAT(N-1))
           DO 51  I=1,M
           II=I-1
51         PRINT *,(R(I,J+1),II,J,J=0,M1)
55         FORMAT(1X,5(5(5X,F10.5,'(',I2,',',I2,')',2X),/))
57         CONTINUE
           PRINT 60
60         FORMAT(//,5X,'MULTIPLE REGRESSION AND SELECTED UNIVARIATE',
           1'STATISTICS')
           PRINT 115
           PRINT 62
62         FORMAT(13X,'VARIABLE',19X,'MULTIPLE',23X,'UNIVARIATE',/,14X,'NUM
           1BER',19X,'REGRESSION',22X,'STATISTICS',/,31X,'SLOPE',10X,'STD.E
           2RROR',11X,'MEAN',7X,'STD.DEVIATION')
           PRINT 115
           PRINT 65, XBAR(1),S(1,1),B(1),SER(1),XBAR(2),S(2,2)
65         FORMAT(5X,'DEPENDANT',17X,'...',14X,'...',3X,2F17.4,/5X,'INDEPEN
           1DENT    1',4F17.4)
           IF(M1-1)  82,82,69
69         CONTINUE
           DO 70 I=2,M1
70         PRINT 80,I,B(I),SER(I),XBAR(I+1),S(I+1,I+1)
80         FORMAT(18X,I2,4F17.4)
82         PRINT 115
           PRINT 85 ,AA,R2,SEE,F
           PRINT 115
85         FORMAT(5X,'INTERCEPT=',F9.4,3X,'MULT.R-SQUARED=',F7.4,3X,'STD.ER
           1ROR OF EST.=',2x,F9.4,'F=',F10.4)
           PRINT 90
90         FORMAT(/,5X,'ACTUAL AND ESTIMATED VALUES OF DEPENDANT VARIABLE',
           1//,13X,'ACTUAL',9X,'ESTIMATED',9X,'RESIDUAL'/)
95         DO 100 I=1,N
100        PRINT 110, I, X(1,I), YHAT(I), YRES(I)
110        FORMAT(5X,I2,F13.5,2F17.5)
115        FORMAT(5X,'---------------------------------------------------
           1-------------------------------------')
120        CONTINUE
           STOP
           END
C          ---------------------------------------------------------------
C
           SUBROUTINE STREG(M,N,X,XBAR,S,A,AA,B,SEE,YHAT,YRES,R2,F,SER,SSE)
C
C          This SUBROUTINE computes the Beta vector for linear regression
C            It also calculates the standard errors of each Betak,k=1,2,..K
C            and the standard deviation of each variable. In addition the
C            program calculates the Multiple Correlation Coefficient R2,
C            the standard error of estimate, and the F-ratio. Also, the
C            actual and the estimated values of the dependent variables
C            alongwith the sample error(or residual) vector e* are computed
```

```
C         The inverse of the matrix x^x is also shown.
C        Subroutine STREG also uses Subroutines MEAN , COVAR , INVS.
C        Description of arguments in Subroutine STREG :
C        M         TOTAL NUMBER OF VARIABLES(DEPENDENT+INDEPENDENT)
C        N         TOTAL NUMBER OF OBSERVATIONS ON EACH VARIABLE
C        X         DATA MATRIX
C        XBAR      VECTOR OF MEANS
C        S         COVARIATION MATRIX
C        A         X^X BEFORE INVERSION, (X^X)INVERSE AFTER INVERSION
C        AA        INTERCEPT
C        B         VECTOR OF SLOPES
C        SEE       STANDARD ERROR OF ESTIMATE
C        YHAT      VECTOR OF ESTIMATED VALUES OF DEPENDENT VARIABLE
C        R2        MULTIPLE CORRELATION COEFFICIENT
C        YRES      VECTOR OF RESIDUALS, OR ERRORS
C        F         F-RATIO
C        SER       VECTOR OF STANDARD ERRORS FOR THE SLOPES
C        SSE       SUM OF THE SQUARED ERRORS
C        ------------------------------------------------------------
         DIMENSION X(50,100),XBAR(50),S(50,50),A(50,50),B(50)
         DIMENSION YHAT(100), YRES(100),SER(50)
         CALL  MEAN(M,N,X,XBAR)
         M1=M-1
         CALL  COVAR(M,N,X,S,XBAR)
         DO 20 I=1,M1
         DO 20 J=1,M1
20       A(I,J)=S(I+1,J+1)

         CALL INVS(A,M1)
         DO 25 I=1,M1
         B(I)=0.0
         DO 25 J=1,M1
25       B(I)=B(I)+S(1,J+1)*A(J,I)
         AA=0.0
         DO 27 I=1,M1
27       AA=AA+XBAR(I+1)*B(I)
         AA=XBAR(1)-AA
         SSE=0.0
         DO 35 I=1,N
         YHAT(I)=0.0
         DO 30 J=2,M
30       YHAT(I)=YHAT(I)+B(J-1)*X(J,I)
         YHAT(I)=YHAT(I)+AA
         YRES(I)=X(1,I)-YHAT(I)
35       SSE=SSE+YRES(I)*YRES(I)
         R2=(S(1,1)-SSE)/S(1,1)
         F = (R2/FLOAT(M1))/((1.0-R2)/FLOAT(N-M))
         SEE=SQRT(SSE/FLOAT(N-M))
         DO 52 I=1,M1
52       SER(I)=SEE*SQRT(A(I,I))
         RETURN
         END
C        ------------------------------------------------------------
         SUBROUTINE  MEAN(M,N,X,XBAR)
C
C        This Subroutine computes the vector of sample means XBAR from a
C          matrix of observations X(M,N) ,which has M variables with N
C          observations on each variable. TXBAR contains M Means.
         DIMENSION X(50,100), XBAR(50)
         DO 20 I=1,M
         SUM=0.0
```

```
      DO 10 J=1,N
   10 SUM=SUM+X(I,J)
   20 XBAR(I)=SUM/FLOAT(N)
      RETURN
      END
C     ------------------------------------------------------------------
      SUBROUTINE  COVAR (M,N,X,S,XBAR)
C
C     This Subroutine computes the matrix x^x from the matrix X.
C                  x = X - XBAR
C       The M*M matrix S is x^x upon exit.
C       To convert x^x into the sample covariance matrix, one needs
C       only to divide each element of S by (n-1).
      DIMENSION X(50,100),S(50,50),XBAR(50)
      DO 20 I=1,M
      DO 20 K=I,M
      SIK=0.0
      DO 10 J=1,N
   10 SIK=SIK+(X(I,J)-XBAR(I))*(X(K,J)-XBAR(K))
      S(I,K)=SIK
   20 S(K,I)=SIK
      RETURN
      END
C     ------------------------------------------------------------------
      SUBROUTINE CORR(M,S,R)
C
C     This Subroutine computes the correlation matrix R from either
C       x^x or the covariane matrix, S. The elements of R are defined
C       by     rij = sij/SQRT(sii.sjj) ; sij are the elements of S.
      DIMENSION S(50,50),R(50,50)
      R(1,1)=1.0
      DO 10 J=2,M
      R(J,J)=1.0
      J1=J-1
      DO 10 I=1,J1
      R(I,J)=S(I,J)/SQRT(S(I,I)*S(J,J))
   10 R(J,I)=R(I,J)
      RETURN
      END
C     ------------------------------------------------------------------
      SUBROUTINE INVS(A,M)
C
C     This Subroutine inverts a matrix by sweeping. The matrix to be
C       inverted need not be symmetric, but it must be square . The
C       matrix is destroyed upon inversion. The matrix A must be non-
C       singular and cannot have any zeros on its main diagonal.
      DIMENSION A(50,50)
      DO 20 K=1,M
      A(K,K)=-1.0/A(K,K)
      DO 5 I=1,M
      IF(I-K) 3,5,3
    3 A(I,K)=-A(I,K)*A(K,K)
    5 CONTINUE
      DO 10 I=1,M
      DO 10 J=1,M
      IF((I-K)*(J-K))  9,10,9
    9 A(I,J)=A(I,J)-A(I,K)*A(K,J)
   10 CONTINUE
      DO 20 J=1,M
      IF(J-K) 18,20,18
   18 A(K,J)=-A(K,J)*A(K,K)
```

```
20      CONTINUE
        DO 25 I=1,M
        DO 25 J=1,M
25      A(I,J)=-A(I,J)
        RETURN
        END
C       ------------------------------------------------------------
```

APPENDIX IX

FORTRAN PROGRAMS FOR THE OPTIMIZATION OF MULTIVARIABLE UNCONSTRAINED FUNCTIONS

K R A F T   P U L P I N G   O P T I M I Z A T I O N

The regression models for kraft pulping can be used to locate the optimum pulping conditions necessary to give the pulp of desired qualities (specifications). Thus it will require the solution of a multivariable optimization problem with inequality constraints. In multivariable constrained problems, the various optimization methods differ only in the way in which they find the feasible point and the feasible direction. A feasible point is one that satisfies all the constraints and a feasible direction is the direction of improvement in the objective function. Two methods have been used in this study:

(1) "Constrained Rosenbrock Method" -- a gradient method and
(2) "Complex Method of Box" -- a nongradient method.

MULTIVARIABLE CONSTRAINED OPTIMIZATION PROGRAMS

These two programs find the maximum of a multivariable, nonlinear function subject to nonlinear inequality constraints:

Maximize F(x1,x2, ...,M)
Subject to Gk <= Xk <= Hk , k=1,2, ...,M

The implicit variables x(N+1),.....,XM are dependent functions of the explicit independent variables x1,x2,....,xN. The upper and lower constraints Hk and Gk are either constants or functions of the independent variables.

In this study the objective function F(pulp yield / burst index / tear index) is a function of 5 explicit independent variables: chemical charge(x1), temperature(x2), sulfidity(x3), liquor-to-wood ratio(x4),and time(x5). The implicit variables are either one, two or three of the regression equations (functions) for Kappa number, burst index, tear index and yield excepting the objective function itself. The upper and lower constraints Hk and Gk are all constants.

```
-------------------------------------------------------------------
   C O N S T R A I N E D   R O S E N B R O C K   M E T H O D

        MULTIVARIABLE CONSTRAINED MAXIMIZATION PROGRAM
-------------------------------------------------------------------
This method is a sequential search technique for non-linear
objective functions subject to non-linear inequality constraints
and does not require any derivatives.

        The procedure requires a starting point that satisfies
the constraints and does not lie in the boundry zones. The
algorithm then proceeds as per a unconstrained Rosenbrock
procedure until convergence is reached or a boundry zone in the
vicinity of the constraints is entered.
 The unconstrained Rosenbrock procedure proceeds as follows:
1. A starting point and initial step sizes Si, i=1,2,...,N, are
   picked and the objective functions evaluated.
2. The first variable X1 is stepped a distance S1,  parallel to
   the axis, and the function evaluated. If the value of F incr-
   eases(maximization), the move is termed a success and S1
   increased by a factor alpha, alpha>=1.0. If the value of F
   decreases the move is termed a failure and S1 decreased by
   a factor beta, 0<beta<=1.0, and the direction of movement
   reversed.
3. The next variable, Xi, is in turn stepped a distance Si
   parallel to the axis. The same acceleration or deceleration
   and reversal procedure is followed for all variables in
   consecutive repetitive sequences until a success(increase in
   F) and failure(decrease in F) have been encountered in all
   N directions.
4. The axes are then rotated in such a way that the direction of
   search is orthogonal to the first and is determined by
   normalized direction vectors from the previous stage.
5. Search is made in each of the X directions using the new
   coordinate axes.

        The following additional steps are carried out after e
   each function evaluation for the Constrained Rosenbrock
   Algorithm:
1. The boundry zones are defined as follows:
         Lower Zone: Gk <= Xk <= (Gk+(Hk-Gk). 10E-04)
         Upper Zone: Hk >= Xk >= (Hk-(Hk-Gk). 10E-04)
   Define by F0 the current best objective function value for a
   point where the constraints are satisfied, and F* the current
   best objective function value for a point where the
   constraints are satisfied and in addition the boundary zones
   are not violated. F0 and F* are initially set equal to the o
   objective function value at the starting point.
2. If the current point objective function evaluation, F, is
   worse than F0 or if the constraints are violated, the trial
   is a failure and the unconstrained procedure is continued.
3. If the current point lies within the boundary zone, the
   objective function is modified as follows:
         F(new)=F(old)-(F(old)-F*)(3*Lam-4*Lam**2+2*Lam**3)
   where
         Lam = (distance into boundary zone)/(width of boundary
                                                          zone)
             = (Gk+(Hk-Gk).10E-04 -Xk)/((Hk-Gk).10E-04)
                                                 (lower zone)
             = (Xk-(Hk-(Hk-Gk).10E-04))/((Hk-Gk).10E-04)
```

```
                                               (upper zone)
   At the inner edge of the boundary zone Lam=0,{F(new)=F(old)}.
   At the constraint, Lam=1 and thus F(new)=F*. Thus the
   function value is replaced by the best current function value
   in the feasible region and not in a boundary zone. For a
   function which improves as the constraint is approached, the
   modified function has an optimum in the boundary zone.
4. If an improvement in the objective function has been obtained
   without violating the boundary zones or constraints, F* is
   set equal to F0 and the procedure continued.
5. The search procedure is terminated when the convergence
   criteria is satisfied.
-----------------------------------------------------------------
DESCRIPYION OF PARAMETERS ...
M          PROBLEM CONTROLLER; +1 FOR MAXIMIZATION,
           -1 FOR MINIMIZATION.
P          NUMBER OF VARIABLES
K          POINT INDEX
L          NUMBER OF VARIABLES + IMPLICT CONSTRAINTS
LOOPY      MAXIMUM NUMBER OF STAGES TO BE CALCULATED
PR         PRINTING CONTROLLER(NUMBER OF STAGES BETWEEN OUTPUTS)
ND         STAGE CONTROLLER, 1 FOR STORAGE IN DA, 0 FOR NO STORAGE
DA         GENERAL STORAGE VECTOR
NDATA      NUMBER OF DATA POINTS TO BE READ IN DA
NPAR       DIMENSION LIMIT IN SUBROUTINES
E          VECTOR OF INITIAL STEP SIZES
X          VECTOR FOR INITIAL GUESSES FOR VARIABLE X
N          DIMENSION LIMIT IN SUBROUTINES
NSTEP      CONTROL ON STEP SIZES FOR EACH ROTATION; 0 FOR ORIGINAL
           STEP SIZES, 1 FOR STEP SIZES FROM PREVIOUS ROTATION
V          DIRECTION VECTOR
DELY       ERROR IN OBJECTIVE FUNTION(DIFFERENCE BETWEEN PRIVIOUS
           AND CURRENT VALUES OF THE OBJECTIVE FUNCTION
-----------------------------------------------------------------
FUNTION SUBPROGRAMS...
FUNCTION F(X,DA,N,NPAR)  SPECIFIES OBJECTIVE FUNCTION
FUNCTION CX(X,DA,N,NPAR,K)  SPECIFIES FUNCTION TO BE CONSTRAINED
FUNCTION CG(X,DA,N,NPAR,K)  SPECIFIES LOWER BOUND OF CONSTRAINTS
FUNCTION CH(X,DA,N,NPAR,K)  SPECIFIES UPPER BOUND OF CONSTRAINTS
-----------------------------------------------------------------
DIMENSION STATEMENT
      DIMENSION  X(8),E(5),V(5,5),SA(5),D(5),G(8),H(8),AL(8),PH(8),
     1A(8,8),B(8,8),BX(8),DA(1),VV(8,8),EINT(5),VM(8)
      COMMON KOUNT
      INTEGER P,PR,R,C
      REAL LC
      READ(1,*),  M,P,L,LOOPY,PR,ND,NDATA,NSTEP
10    DO  100  K=1,P
      READ(1,*),  X(K)
100   CONTINUE
      DO  200  J=1,P
      READ (1,*),  E(J)
200   CONTINUE
      PRINT 13
13    FORMAT(1H1,20X,'O P T I M I Z A T I O N  O F  T H E  K R A F T
     1  P U L P I N I G  P R O C E S S ',///,38X,'CONSTRAINED ROSENBR
     2OCK ALGORITHM',//,20X,'MULTIVARIABLE NONLINEAR FUNCTION SUBJECT
     3ED TO NON LINEEAR INEQUALITY CONSTRAINTS',//)
      IF(ND-1)  30,20,30
20    DO  300  KA=1,NDATA
      READ(1,*),  DA(KA)
```

```
300     CONTINUE
30      LAP = PR-1
        LOOP = 0
        ISW = 0
        INIT = 0
        KOUNT = 0
        TERM = 0.0
        DELY = 1.0E-10
        F1 = 0.0
        NPAR = NDATA
        N = L
        DO  40  K=1,L
40      AL(K) = (CH(X,DA,N,NPAR,K)-CG(X,DA,N,NPAR,K))*0.0001
        DO  60  I=1,P
        DO  60  J=1,P
        V(I,J) = 0.0
        IF(I-J)  60,61,60
61      V(I,J) = 1.0
60      CONTINUE
        DO  65  KK=1,P
        EINT(KK) = E(KK)
65      CONTINUE
1000    DO  70  J=1,P
        IF(NSTEP .EQ. 0)  E(J) = EINT(J)
        SA(J) = 2.0
70      D(J) = 0.0
        FBEST = F1
80      I= 1
        IF(INIT  .EQ. 0)  GO TO 120
90      DO  110  K=1,P
110     X(K) = X(K)+E(I)*V(I,K)
        DO  50  K=1,L
50      H(K) = F0
120     F1 = F(X,DA,N,NPAR)
        F1 = FLOAT(M)*F1
        IF(ISW .EQ. 0)  F0=F1
        ISW = 1
        IF(ABS(FBEST-F1)-DELY)  122,122,125
122     TERM =1.0
        GO TO  450
125     CONTINUE
        J = 1
130     XC = CX(X,DA,N,NPAR,J)
        LC = CG(X,DA,N,NPAR,J)
        UC = CH(X,DA,N,NPAR,J)
        IF(XC .LE. LC)  GO TO  420
        IF(XC .GE. UC)  GO TO  420
        IF(F1 .LT. F0)  GO TO  420
        IF(XC .LT. LC+AL(J))  GO TO  140
        IF(XC .GT. UC-AL(J))  GO TO  140
        H(J) = F0
        GO TO  210
140     CONTINUE
        BW =AL(J)
        IF(XC .LE. LC .OR. UC .LE. XC)  GO TO  150
        IF(LC .LT. XC .AND. XC .LT. LC+BW)  GO TO  160
        IF(UC-BW .LT. XC .AND. XC .LT. UC)  GO TO  170
        PH(J) = 1.0
        GO TO  210
150     PH(J) = 0.0
        GO TO  190
```

```
160     PW = (LC+BW-XC)/BW
        GO TO  180
170     PW = (XC-UC+BW)/BW
180     PH(J) = 1.0-3.0*PW+4.0*PW*PW-2.0*PW*PW*PW
190     F1 = H(J)+(F1-H(J))*PH(J)
210     CONTINUE
        IF(J .EQ. L)  GO TO  220
        J = J+1
        GO TO  130
220     INIT = 1
        IF(F1 .LT. F0) GO TO  420
        D(I) = D(I) + E(I)
        E(I) = 3.0*E(I)
        F0 = F1
        IF(SA(I) .GE. 1.5)  SA(I) = 1.0
230     DO  240  JJ=1,P
        IF(SA(JJ) .GE. 0.5)  GO TO 440
240     CONTINUE
C                 Axes  Rotation
        DO  250  R=1,P
        DO  250  C=1,P
250     VV(C,R) = 0.0
        DO  260  R=1,P
        KR = R
        DO  260  C=1,P
        DO  265  K=KR,P
265     VV(R,C) = D(K)*V(K,C)+VV(R,C)
260     B(R,C) = VV(R,C)
        BMAG= 0.0
        DO  280   C=1,P
        BMAG = BMAG+B(1,C)*B(1,C)
280     CONTINUE
        BMAG = SQRT(BMAG)
        BX(1) = BMAG
        DO  310  C=1,P
310     V(1,C) = B(1,C)/BMAG
        DO  390  R=2,P
        IR = R-1
        DO  390  C=1,P
        SUMVM = 0.0
        DO  320  KK=1,IR
        SUMAV = 0.0
        DO  330  KJ=1,P
330     SUMAV = SUMAV+VV(R,KJ)*V(KK,KJ)
320     SUMVM = SUMAV*V(KK,C)+SUMVM
390     B(R,C) = VV(R,C)-SUMVM
        DO  340  R=2,P
        BBMAG = 0.0
        DO  350  K=1,P
350     BBMAG = BBMAG+B(R,K)*B(R,K)
        BBMAG = SQRT(BBMAG)
        DO  340  C=1,P
340     V(R,C) = B(R,C)/BBMAG
        LOOP = LOOP+1
        LAP = LAP+1
        IF(LAP .EQ. PR)  GO TO  450
        GO TO  1000
420     IF(INIT .EQ. 0)  GO TO  450
        DO  430  IX=1,P
430     X(IX) = X(IX)-E(I)*V(I,IX)
```

```
      E(I) = -0.5*E(I)
      IF(SA(I) .LT. 1.5)  SA(I) =0.0
      GO TO  230
440   CONTINUE
      IF(I .EQ. P)  GO TO  80
      I =I+1
      GO TO  90
450   PRINT 3
3     FORMAT(///,10X,'STAGE',8X,'FUNCTION',12X,'PROGRESS',9X,'LATERAL
     1PROGRESS',/)
      PRINT 4,   LOOP,F0,BMAG,BBMAG
4     FORMAT(10X,I4,3E20.8)
      PRINT 14, KOUNT
14    FORMAT(/,10X,'NUMBER OF FUNCTION EVALUATIONS =',I8)
      PRINT 5
5     FORMAT(/,10X,'VALUES OF X AT THIS STAGE')
C               Print Current Values of X
      PRINT 6,   (JM,X(JM),JM=1,P)
6     FORMAT(/,10X,5(1X,'X(',I1,') = ',E10.5,4X))
      LAP = 0
      IF(INIT .EQ. 0 )  GO TO  470
      IF(TERM .EQ. 1.0)  GO TO 480
      IF(LOOP .GE. LOOPY) GO TO 480
      GO TO 1000
470   PRINT 7
7     FORMAT(///,10X,'THE STARTING POINT MUST NOT VOILATE THE CONSTAIN
     1TS. IT APPEARS TO HAVE DONE SO.')
480   CONTINUE
490   PRINT 8
8     FORMAT(///,10X,'FINAL DIRECTION VECTOR MATRIX')
      DO  500  J=1,P
500   PRINT 9,   (J,I,V(J,I),I=1,P)
9     FORMAT(/,5X,5(1X,'V(',I1,',',I1') =',E12.6,2X))
      PRINT 11
11    FORMAT(//,10X,'FINAL STEP SIZES')
      PRINT 12,   (J,E(J),J=1,P)
12    FORMAT(/,10X,5(1X,'S(',I1,') = ',E12.6,2X))
      IF(L .EQ. P)  STOP
      JLP = P+1
      PRINT 17
      DO 19  JL = JLP,L
      PRINT  16,   JL , X(JL)
19    CONTINUE
16    FORMAT(/,10X,'X(',I1,') =',F8.3)
17    FORMAT(//,10X,'VALUES OF THE CONSTRAINTS AT THE OPTIMUM',/)
      STOP
      END
C     ----------------------------------------------------------------
C
      FUNCTION  F(X,DA,N,NPAR)
C     FUNCTION F(X,DA,N,NPAR) SPECIFIES THE OBJECTIVE FUNCTION.
C
C     K R A F T   P U L P I G   O F   P I N E
C
C     The objective is to maximize Tear Index of the pulp.
C     DESCRIPTION OF PARAMETERS ...
C     X(1)   PERCENT ACTIVE ALKALI , CHEMICAL CHARGE ASNA2O
C     X(2)    MAX. COOKING TEMPARATURE , DEGREE C
C     X(3)    PERCENT SULFIDITY.
C     X(4)    LIQUOR-TO-WOOD RATIO.
C     X(5)    COOKING TIME, MIN.
```

```
      DIMENSION  X(8) , DA(1)
      COMMON  KOUNT
C           Changing original variables into their coded forms:
      X1 = (X(1)-17.5)/1.5
      X2 = (X(2)-170.0)/5.0
      X3 = (X(3)-25.0)/5.0
      X4 = (X(4)-3.75)/0.25
      X5 = (X(5)-80.0)/20.0
C
C           TEAR INDEX
C
      F = 12.634+0.270*X1-0.473*X2+0.321*X3+0.188*X4+0.149*X5+0.168*X1
     1*X2-0.064*X1*X3-0.428*X1*X4-0.171*X1*X5+0.096*X2*X3+0.258*X2*X4
     2-0.234*X2*X5-0.449*X3*X4-0.158*X3*X5+0.001*X4*X5
C
      KOUNT = KOUNT+1
      RETURN
      END
C     ------------------------------------------------------------------
C
      FUNCTION CX(X,DA,N,NPAR,K)
C     FUNCTION CX  specifies the Functions to be constrainted (Kappa
C                  number, screened pulp yield, and burst index)
      DIMENSION X(8) , DA(1)
      X1 = (X(1)-17.5)/1.5
      X2 = (X(2)-170.0)/5.0
      X3 = (X(3)-25.0)/5.0
      X4 = (X(4)-3.75)/0.25
      X5 = (X(5)-80.0)/20.0
      X11 = X1*X1
      X22 = X2*X2
      X33 = X3*X3
      X44 = X4*X4
      X55 = X5*X5
C
C           PULPP KAPPA NUMBER
      X(6) = 49.618-8.706*X1-9.581*X2-2.731*X3+2.131*X4-4.131*X5+2.306
     1*X1*X2+0.481*X1*X3+1.818*X1*X4-1.490*X1*X5+0.681*X2*X3+1.044*X2
     2*X4+1.606*X2*X5+1.193*X3*X4-2.818*X3*X5-0.156*X4*X5
C           SCREENED PULP YIELD
      X(7) = 44.588-0.461*X1-1.062*X2+1.217*X3+0.110*X4-0.072*X5+0.047
     1*X1*X2+0.290*X1*X3+0.522*X1*X4+0.092*X1*X5-0.528*X2*X3+0.111*X2
     2*X4-0.684*X2*X5+0.001*X3*X4-0.646*X3*X5-0.246*X4*X5
C           BURST INDEX
      X(8) = 6.582+0.052*X1-0.043*X2+0.296*X3+0.059*X4+0.103*X5-0.273*
     1X1*X2+0.103*X1*X3-0.133*X1*X4+0.033*X1*X5+0.011*X2*X3+0.094*X2*
     2X4+0.028*X2*X5-0.157*X3*X4+0.142*X3*X5-0.007*X4*X5
C
      CX =X(K)
      RETURN
      END
C      -----------------------------------------------------------------
      FUNCTION  CG(X,DA,N,NPAR,K)
C     FUNCTION  CG  specifies lower bound of the constraints (Lower
C                   limit of the range of independent pulping variable
C                   and the pulp properties)
      DIMENSION  X(8) , DA(1)
      GO TO (10,20,30,40,50,60,70,75) , K
10    CG = 16.0
      GO TO  80
20    CG = 165.0
```

```
      GO TO  80
30    CG = 20.0
      GO TO  80
40    CG = 3.5
      GO TO  80
50    CG = 60.0
      GO TO  80
60    CG = 35.0
      GO TO  80
70    CG = 41.0
      GO TO  80
75    CG = 6.80
80    CONTINUE
      RETURN
      END
C     ------------------------------------------------------------------
C
      FUNCTION  CH(X,DA,N,NPAR,K)
C     FUNCTION  CH  specifies the upper bound of the constraints
C                   (Upper limit of the range of independent pulping
C                   variables and the pulp properties)
      DIMENSION X(8) , DA(1)
      GO TO (10,20,30,40,50,60,70,75) , K
10    CH = 19.0
      GO TO  80
20    CH = 175.0
      GO TO  80
30    CH = 30.0
      GO TO  80
40    CH = 4.0
      GO TO  80
50    CH = 100.0
      GO TO  80
60    CH = 55.0
      GO TO  80
70    CH = 48.0
      GO TO  80
75    CH = 8.40
80    CONTINUE
      RETURN
      END
C     ------------------------------------------------------------------
```

```
C     ----------------------------------------------------------------------
C
C           C O M P L E X   M E T H O D   O F   B O X
C
C        MULTIVARIBLE  CONSTRAINTED  MAXIMIZATION  PROGRAM
C     ----------------------------------------------------------------------
C     This method is a sequential search technique for non-linear
C     objective  functions and does  not require any derivatives.
C
C     DESCRIPTION OF PARAMETERS---
C     N        NUMBER OF EXPLICIT INDEPENDENT VARIABLES  (5)
C     M        NUMBER OF SETS OF CONSTRAITNTS
C     K        NUMBER OF POINTS IN THE COMPLEX (N+1 =6)
C     ITMAX    MAXIMUM NUMBER OF ITERATIONS
C     IC       NUMBER OF IMPLICIT VARIABLES
C     ALPHA    REFLECTION FACTOR  (1.3)
C     BETA     CONVERGENCE PARAMETER (0.10)
C     GAMMA    CONVERGENCE PARAMETER  (5)
C     DELTA    EXPLICIT CONSTRAINT VIOLATION CORRECTION
C     IPRINT   CODE TO CONTROL PRINTING OF INTERMIDIATE ITERATIONS
C       IPRINT=1 CAUSES INTERMIDIATE VALUES TO PRINT ON EACH ITERATION
C       IPRINT=0 SUPRESSES PRINTING UNTIL FINAL SOLUTION IS OBTAINED
C     X        INDEPENDENT VARIABLE.
C     R        RANDOM NUMBERS BETWEEN 0 AND 1
C     F        OBJECTIVE FUNCTION                   ( FUNC )
C     IT       ITERATION INDEX                      ( BOXC )
C     IEV1     INDEX OF POINT MINIMUM FUNCTION VALUE (BOXC,CHECK)
C     IEV2     INDEX OF POINT WITH MAXIMUM FUNCTION VALUES ( BOXC)
C     G        LOWER CONSTRAINT                     ( CONST )
C     H        UPPER CONSTRAINT                     ( CONST )
C     XC       CENTROID                              ( CNTRD )
C     I        PRINT INDEX                           ( BOXC )
C     KODE     KEY USED TO DETERMINE IF IMPLICIT CONSTAINTS ARE PROVIDE
C                                                      ( BOXC, CHECK )
C     K1       DO LOOP LIMIT                           ( BOXC )
C     ----------------------------------------------------------------------
C     SUBROUTINES >>>
C     SUBROUTINE BOXC      CALLED FROM THE MAIN PROGRAM COORDINATES ALL
C                          SPECIAL PURPOSE SUBROUTINES.
C     SUBROUTINE CHECK     CHECKS ALL POINTS AGAINST EXPLICIT AND
C                          IMPLICIT CONSTRAINTS AND APPLIES CORRECTION
C                          IF VIOLATIONS ARE FOUND.
C     SUBROUTINE CNTRD     CALCULATES THE CENTROID OF POINTS.
C     SUBROUTINE FUNC      SPECIFIES OBJECTIVE FUNCTION.
C     SUBROUTINE CONST     SPECIFIES EXPLICIT AND IMPLICIT CONSTRAINT
C                          LIMITS, ORDER EXPLICIT CONSTRAINTS FIRST.
C     ----------------------------------------------------------------------
C     Main Program for the Complex Method of Box
C
      DIMENSION  X(6,8) , R(6,5) , F(6) , G(8) , H(8) , XC(5)
      INTEGER GAMMA
C            Reading input data:
      READ(1,*), N,M,K,ITMAX,IC,IPRINT
      READ(1,*), ALPHA , BETA , GAMMA
      DELTA = 0.001
      READ(1,*),  (X(1,J) , J=1,N)
      DO  100  II=2,K
      READ(1,*),  (R(II,JJ) , JJ=1,N)
100   CONTINUE
C            Printing input data:
      PRINT 10
```

```
10      FORMAT(///,7X,'O P T I M I Z A T I O N  O F  T H E  K R A F T  P
       1 U L P I N G  P R O C E S S',//,25X,'C O M P L E X  M E T H O D
       2  O F  B O X',/)
        PRINT 18
18      FORMAT(/,5X,'PARAMETERS:-')
        PRINT 11,  N,M,K,ITMAX,IC,ALPHA,BETA,GAMMA,DELTA
11      FORMAT(//,5X,'N =',I2,5X,'M =',I2,5X,'K =',I2,5X,'ITMAX =',I5,
       15X,'IC =',I2,//,5X,'ALPHA =',F5.2,5X,'BETA =',F7.3,5X,'GAMMA ='
       2,I2,5X,'DELTA = ',F6.4,//)
        IF(IPRINT)  40 , 50 , 40
40      PRINT 12
12      FORMAT(//,5X,'RANDOM NUMBERS:-',/)
        DO  200 J=2,K
        PRINT 13,   (J,I,R(J,I),I=1,N)
13      FORMAT(/,5(5X,'R(',I1,',',I1,') = ',F6.4,2X))
200     CONTINUE
50      CALL BOXC(N,M,K,ITMAX,ALPHA,BETA,GAMMA,DELTA,X,R,F,IT,IEV2,
       1G,H,XC,IPRINT)
C             Printing optimization results:
        IF(IT-ITMAX)  20 , 20 , 30
20      PRINT 14,  F(IEV2)
14      FORMAT(//5X,'MAXIMUM TOTAL PULP YIELD,PERCENT =',F8.3,/)
        PRINT 15
15      FORMAT(//5X,'OPTIMUM PROCESS VARIABLE VALUES:-'/)
        PRINT 16,   (X(IEV2,I),I=1,N)
16      FORMAT(/,5X,'ACTIVE ALKALI,PERCENT AS Na2O ON O.D.BASIS='
       1,F12.5//5X,'MAXIMUM COOKING TEMPRATURE,DEGREE C='F12.5//
       25X,'SULFIDITY,PERCENT=',F12.5//5X,'LIQUID-TO-WOOD RATIO  ='
       3,F12.5//5X,'TIME-AT-TEMPRATURE,MIN.=',F12.5//)
        NN = N+1
        PRINT 21
        PRINT 19,   (X(IEV2,I) , I =NN,M)
        GO TO  999
30      PRINT 17,   ITMAX
17      FORMAT(///,5X,'THE NUMBER OF ITERATIONS HAS EXCEEDED',I4,10X,
       1'PROGRAM TERMINATED'/)
19      FORMAT(/,5X,'BURST INDEX = ',F10.4,/,5X,'TEAR INDEX = ',F10.4)
21      FORMAT(/,5X,'PULP PROPERTIES (CONSTRAINTS) :-',/)
999     STOP
        END
C       ------------------------------------------------------------
C
        SUBROUTINE BOXC(N,M,K,ITMAX,ALPHA,BETA,GAMMA,DELTA,X,R,F,IT,
       1IEV2,G,H,XC,IP)
C
C       SUBROUTINE BOXC  CALLED FROM MAIN PROGRAM AND COORDINATES
C       ALL SPECIAL PURPOSE SUBROUTINES (CHECK,CNTRD,FUNC,CONST)
C       ARGUMENT LIST---
C       IT      = ITERATION INDEX
C       IEV1    = INDEX OF POINT WITH MINIMUM FUNCTION VALUE.
C       IEV2    = INDEX OF POINT WITH MAXIMUM FUNCTION VALUE.
C       I       = POINT INDEX.
C       KODE    = CONTROL KEY USED TO DETERMINE IF IMPLICIT CONSTRAINTS
C                 ARE PROVIDED.
C       K1      = DO LOOP LIMIT.
C       ALL OTHER PRECISELY DEFINED IN MAIN PROGRAM.
C
        DIMENSION  X(K,M) , R(K,N) , F(K) , G(K) , H(M) , XC(N)
        INTEGER  GAMMA
        IT=1
        KODE=0
```

```
      IF(M-N) 20 , 20 , 10
10    KODE =1
20    CONTINUE
      DO  40  II=2,K
      DO  30  J=1,N
30    X(II,J) = 0.0
40    CONTINUE
C           Calculate complex points and check against constraints.
      DO 65  II=2,K
      DO  50  J=1,N
      I=II
      CALL CONST(N,M,K,X,G,H,I)
      X(II,J)=G(J)+R(II,J)*(H(J)-G(J))
50    CONTINUE
      K1=II
      CALL  CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
      IF(II-2)  51 , 51 , 55
51    IF(IPRINT)  52 , 65 , 52
52    PRINT 18
18    FORMAT(//,5X,'COORDINATES OF INITIAL COMPLEX'/)
      ID=1
      PRINT 19,  (ID,J,X(ID,J),J=1,N)
19    FORMAT(/,3(5X,'X(',I2,',',I2,') = ',F13.6))
55    IF(IPRINT)  56 , 65 , 56
56    PRINT 19,  (II,J,X(II,J),J=1,N)
65    CONTINUE
      K1=K
      DO  70  I=1,K
      CALL  FUNC(N,M,K,X,F,I)
70    CONTINUE
      KOUNT=1
      IA=0
C           Find point with lowest Function value.
      IF(IPRINT)  72 , 80 , 72
72    PRINT 21
21    FORMAT(/,5X,'VALUES OF THE FUNCTION')
      PRINT 22,  (J,F(J),J=1,K)
22    FORMAT(/,3(5X,'F(',I2,') = ',F13.6))
80    IEV1=1
      DO  100  ICM=2,K
      IF(F(IEV1)-F(ICM))  100 , 100, 90
90    IEV1=ICM
100   CONTINUE
C           Find point with highest Function value.
      IEV2=1
      DO  120  ICM=2,K
      IF(F(IEV2)-F(ICM))  110 , 110 , 120
110   IEV2=ICM
120   CONTINUE
C           Check convergence criteria.
      IF(F(IEV2)-(F(IEV1)+BETA))  140 , 130 , 130
130   KOUNT=1
      GO TO   150
140   KOUNT = KOUNT+1
      IF(KOUNT-GAMMA)  150 , 240 , 240
C           Replace point with lowest Function value.
150   CALL CNTRD(N,M,K,IEV1,I,XC,X,K1)
      DO  160  JJ=1,N
160   X(IEV1,JJ)=(1.0+ALPHA)*(XC(JJ))-ALPHA*(X(IEV1,JJ))
      I=IEV1
      CALL  CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
```

```
      CALL  FUNC(N,M,K,X,F,I)
C           Replace new point if repeats as lowest Function value.
170   IEV2=1
      DO  190  ICM=2,K
      IF(F(IEV2)-F(ICM))  190 , 190 , 180
180   IEV2=ICM
190   CONTINUE
      IF(IEV2-IEV1)  220 , 200 ,220
200   DO  210  JJ=1,N
      X(IEV1,JJ)=(X(IEV1,JJ)+XC(JJ))/2.0
210   CONTINUE
      I=IEV1
      CALL  CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
      CALL  FUNC(N,M,K,X,F,I)
      GO TO 170
220   CONTINUE
      IF(IPRINT)                221,228,221
221   IF(IT-1)                221,230,222
222   IF((IT/10*10)  .NE.  IT)  GO TO 228
230   PRINT 23,  IT
23    FORMAT(//,5X,'ITERATION NUMBER',I5)
      PRINT 24
24    FORMAT(/,5X,'COORDINATES OF CORRECTED POINTS')
      PRINT 19,  (IEV1,JC,X(IEV1,JC),JC=1,N)
      PRINT 21
      PRINT 22, (I,F(I),I=1,K)
      PRINT 25
25    FORMAT(/,5X,'COORDINATES OF THE CENTROID')
      PRINT 26,  (JC,XC(JC),JC=1,N)
26    FORMAT(/,3(5X,'X(',I2,') = ',F14.6,4X))
228   IT=IT+1
      IF(IT-ITMAX)  80 , 80 , 240
240   RETURN
      END
C     ------------------------------------------------------------------
C
      SUBROUTINE CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
C
C     SUBROUTINE CHECK  CHECKS ALL POINTS AGAINST EXPLICIT
C     CONSTRAINTS AND APPLIES CORRECTIONS IF VIOLATIONS ARE FOUND.
C     ALL THE ARGUMENTS ARE DEFINED IN THE MAIN PROGRAM AND BOXC.
C
      DIMENSION X(6,8) , G(8) , H(8) , XC(5)
10    KT=0
      CALL  CONST(N,M,K,X,G,H,I)
C           Check against explicit constraints.
      DO  50  J=1,N
      IF(X(I,J)-G(J))  20 , 20 , 30
20    X(I,J) = G(J)+DELTA
      GO TO  50
30    IF(H(J)-X(I,J))  40 , 40 , 50
40    X(I,J) = H(J) - DELTA
50    CONTINUE
      IF(KODE)  110,110,60
C           Check against implicit constraints.
60    NN=N+1
      DO  100  J=NN,M
      CALL  CONST(N,M,K,X,G,H,I)
      IF(X(I,J)-G(J))  80 , 70 , 70
70    IF(H(J)-X(I,J))  80 , 100 , 100
80    IEV1=I
```

```
      KT=1
      CALL CNTRD(N,M,K,IEV1,I,XC,X,K1)
      DO  90  JJ=1,N
      X(I,JJ) = (X(I,JJ)+XC(JJ))/2.0
90    CONTINUE
100   CONTINUE
      IF(KT)  110 , 110 ,10
110   RETURN
      END
C     ------------------------------------------------------------------
C
      SUBROUTINE CNTRD(N,M,K,IEV1,I,XC,X,K1)
C
C     SUBROUTINE CNTRD  CALCULATES THE CENTRROID OF POINTS.
      DIMENSION X(6,8) , XC(5)
      DO  20  J=1,N
      XC(J)=0.0
      DO  10  IL=1,K1
10    XC(J) = XC(J)+X(IL,J)
      RK = FLOAT(K1)
20    XC(J) = (XC(J)-X(IEV1,J))/(RK-1.0)
      RETURN
      END
C     ------------------------------------------------------------
C
      SUBROUTINE  FUNC(N,M,K,X,F,I)
C     THIS SUBROUTINE SPECIFIES OBJECTIVE FUNCTION
C     K R A F T  P U L P I N G  O F  E U C A L Y P T
C     The objective is to obtain maximum pulp yield.
      DIMENSION  X(6,8) , F(6)
C            Changing pulping variables into their coded forms:
      X1 = (X(I,1)-16.0)/1.0
      X2 = (X(I,2)-165.0)/5.0
      X3 = (X(I,3)-21.0)/3.0
      X4 = (X(I,4)-3.6)/0.3
      X5 = (X(I,5)-60.0)/15.0
      X11=X1*X1
      X22=X2*X2
      X33=X3*X3
      X44=X4*X4
      X55=X5*X5
C                       PULP YIELD
      F(I) = 49.5454-1.4125*X1-0.7391*X2-0.2791*X3+0.3941*X4-0.6766*
     1X5-0.4992*X11+0.0295*X22-0.142*X33-0.1929*X44-0.0604*X55-0.2637
     2*X1*X2-0.075*X1*X3-0.4737*X1*X4+0.0299*X1*X5-0.3937*X2*X3+0.942
     34*X2*X4+0.5262*X2*X5-0.4337*X3*X4-0.9474*X3*X5+0.3612*X4*X5
      RETURN
      END
C     ------------------------------------------------------------------
C
      SUBROUTINE CONST(N,M,K,X,G,H,I)
C     This Subroutine specifies explicit(independent pulping variables
C      and implicit(Burst index,Tear index) constraint limit.Explicit
C      constraints first in order.
      DIMENSION  X(6,8) , G(8) , H(8)
      X1  =(X(I,1)-16.00)/1.0
      X2  =(X(I,2)-165.0)/5.0
      X3  =(X(I,3)-21.00)/3.0
      X4  =(X(I,4)-3.600)/0.3
      X5  =(X(I,5)-60.00)/15.0
      X11 =X1*X1
```

```
X22  =X2*X2
X33  =X3*X3
X44  =X4*X4
X55  =X5*X5
            Explicit Constraints
G(1)=   14.0
H(1)=   18.0
G(2)=  155.0
H(2)=  175.0
G(3)=   15.0
H(3)=   27.0
G(4)=    3.0
H(4)=    4.2
G(5)=   30.0
H(5)=   90.0
            Implicit Constraints
                   BURST INDEX
G(6)=  4.40
H(6)=  5.40

X(I,6) = 5.218-0.122*X1+0.206*X2+0.142*X3+0.124*X4+0.080*X5+0.23
18*X11+0.012*X22-0.078*X33+0.131*X44+0.181*X55-0.228*X1*X2-0.104
2*X1*X3-0.028*X1*X4-0.008*X1*X5+0.057*X2*X3-0.067*X2*X4-0.129*X2
3*X5+0.034*X33*X4+0.084*X3*X5-0.037*X4*X5

                   TEAR INDEX
G(7)=  7.80
H(7)=  8.40

X(I,7) = 8.233-0.124*X1-0.103*X2-0.016*X3+0.160*X4-0.375*X5-0.15
11*X11-0.163*X22+0.061*X33-0.047*X44-0.491*X55+0.275*X1*X2+0.136*
2*X1*X3+0.083*X1*X4-0.089*X1*X5-0.319*X2*X3+0.055*X2*X4+0.089*X2
3*X5+0.359*X3*X4+0.278*X3*X5-0.134*X4*X5
RETURN
END
-------------------------------------------------------------------
```

00258